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SERIES A

CONTAINING PAPERS OF A MATHEMATICAL AND
PHYSICAL CHARACTER.

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MINUTES OF MEETINGS OF THE ROYAL SOCIETY.

May 29, 1930.

Sir Ernest RUTHERFORD, O.M., President, in the Chair.

Prof. E. Bailey, Dr. P. A. M. Dirac, Dr. H. W. Dudley, Prof. C. A. Edwards and Prof. R. Robison were admitted into the Society.

Prof. R. Robinson, F.R.S., delivered the Bakerian Lecture on "The Molecular Structure of Strychnine and Brucine."

June 12, 1930.

Sir Ernest RUTHERFORD, O.M., President, in the Chair.

The following papers were read :—

I. Sir Sidney Burrard, F.R.S. "The Geographical Representation of the Mountains of Tibet."

II. E. G. Coker, F.R.S., and G. P. Coleman. "Cleavage Tests in Timber."

III. M. C. Johnson. "Experiments on the Exchange of Energy between Gas, Solid and Adsorbed Layer *in vacuo*." Communicated by S. W. J. Smith, F.R.S.

IV. E. H. Gowan. "The Effect of Ozone on the Temperature of the Upper Atmosphere." Communicated by F. A. Lindemann, F.R.S.

V. A. Müller. "The Crystal Structure of the Normal Paraffins at Temperatures ranging from that of Liquid Air to the Melting Points." Communicated by Sir William Bragg, F.R.S.

VI. H. S. W. Massey. "Remarks on the Anomalous Scattering of α-Particles from the Quantum Mechanical Point of View." Communicated by R. H. Fowler, F.R.S.

VII. H. Jones. "The Energy of Crystal Lattices." Communicated by R. H. Fowler, F.R.S.

VIII. R. H. Dalton. "The Oxidation of Phosphine." Communicated by C. N. Hinshelwood, F.R.S.

IX. F. P. Bowden and E. A. O'Connor. "The Change in the Area and Catalytic Activity of Metallic Surfaces on Passing from the Solid to the Liquid State." Communicated by T. M. Lowry, F.R.S.

X. E. W. R. Steacie and H. N. Campbell. "The Thermal Decomposition of Ethyl Ether on the Surface of Platinum." Communicated by A. S. Eve, F.R.S.

XI. E. T. S. Appleyard. "Experiments on the Excitation of Light by Low Voltage Positive Rays." Communicated by Sir Ernest Rutherford, P.R.S.

XII. G. O. Langstroth. "Relative Intensities of Stark Components in Helium." Communicated by A. S. Eve, F.R.S.

XIII. J. M. Adams. "The Polar Properties of Single Crystals of Ice." Communicated by H. Bateman, F.R.S.

XIV. W. G. Kannuluik. "An Electrical Method of Determining Thermal Conductivities of Metal Wires." Communicated by Sir Ernest Rutherford, P.R.S.

June 19, 1930.

Sir Ernest RUTHERFORD, O.M., President, followed by Sir Henry LYONS, Vice-President and Treasurer, in the Chair.

Prof. H. S. Allen and Prof. G. P. Thomson were admitted into the Society.

The following papers were read:—

I. H. R. Robinson, F.R.S., and C. L. Young. "New Results of the Magnetic Spectroscopy of X-Ray Electrons."

II. F. C. Toy and G. B. Harrison. "Photo-Conductance Phenomena in the Silver Halides and Latent Photographic Image." Communicated by T. Slater Price, F.R.S.

III. C. H. M. Jenkins and M. L. V. Gayler "The Optical Determination of High Metallurgical Temperatures." "The Melting Point of Iron." Communicated by W. Rosenhain, F.R.S.

June 26, 1930.

Sir Ernest RUTHERFORD, O.M., F.R.S., President, in the Chair.

The Right Honorable James Ramsay MacDonald and General The Right Honorable Jan Christiaan Smuts were elected into the Society under Statute 12.

Baron Gerard de Geer and Professor Tullio Levi-Civita were elected Foreign Members of the Society.

I. A. V. Hill, F.R.S., and P. S. Kupalov. "The Vapour Pressure of Muscle."

II. A. V. Hill, F.R.S. "The State of Water in Muscle and Blood, and the Osmotic Behaviour of Muscle."

III. W. Sucksmith. "The Gyromagnetic Effect for Paramagnetic Substances." Communicated by A. P. Chattock, F.R.S.

IV. J. C. McLennan, F.R.S., and R. Turnbull. "The Absorption of Light by Gaseous, Liquid, and Solid Xenon."

V. L. E. S. Eastham. "The Embryology of *Pieris rapæ*.—Organogeny." Communicated by J. S. Gardiner, F.R.S.

VI. E. Sprawson. "On the Histological Evidences of the Organic content and Reactions of Marsupial Enamel. With a Note on Human Enamel." Communicated by W. Bulloch, F.R.S.

VII. A. E. Boycott, F.R.S., C. Diver, S. L. Garstang and F. M. Turner. "The Delayed Inheritance of Sinistrality in *Limnæa peregra* (Mollusca Pulmonata), with notes on the Inheritance of Albinism and shell-shape."

VIII. R. B. Bourdillon, J. H. Gaddum and R. G. C. Jenkins. "The Production of Histamine from Histidine by Ultra-Violet Light and the Absorption Spectra of the Substances." Communicated by H. H. Dale, Sec., R.S.

IX. E. Ponder and J. F. Yeager. "The Use of *n*th Order Equations to describe the Action of Simple Hæmolysyns." Communicated by Sir Edward Sharpey-Schafer, F.R.S.

X. E. Ponder. "The Effect of variations in the Cell Content of Hæmolytic Systems."

XI. E. Ponder. "The Form of the Frequency Distribution of Red Cell Resistance to Saponin."

XII. A. D. Adrian, F.R.S. "The Effects of Injury on Mammalian Nerve Fibres."

XIII. P. A. Buxton. "Evaporation from the Meal-Worm (*Tenebrio*—Coleoptera) and Atmospheric Humidity." Communicated by J. S. Haldane, F.R.S.

XIV. G. Pincus. "Observations on the Living Eggs of the Rabbit." Communicated by F. H. A. Marshall, F.R.S.

XV. R. Deanesly. "The Corpora Lutea of the Mouse, with special reference to Fat Accumulation during the Oestrous Cycle." Communicated by J. P. Hill, F.R.S.

XVI. E. M. Crowther. "The Relationship of Climatic and Geological Factors to the Composition of Soil Clay and the Distribution of Soil Types." Communicated by Sir John Russell, F.R.S.

XVII. M. Hill and A. S. Parkes. "The Relation between the Anterior Pituitary Body and the Gonads.—I and II." Communicated by C. Lovatt Evans, F.R.S.

XVIII. K. Clusius and C. N. Hinshelwood, F.R.S. "Homogeneous Catalysis of Gaseous Reactions.—I and II."

XIX. C. N. Hinshelwood, F.R.S., K. Clusius and G. Hadman. "Homogeneous Catalysis of Gaseous Reactions. III."

XX. R. H. Fowley, F.R.S. "A Possible Explanation of the Selective Photo-electric Effect."

XXI. Lord Rayleigh, F.R.S. "The Ultra-Violet Transmission—Band of Metallic Silver as affected by Temperature."

XXII. L. H. Gray. "The Scattering of Hard γ-Rays." Communicated by Sir Ernest Rutherford, P.R.S.

XXIII. G. Temple. "The Operational Wave Equation and the Zeeman Effect." Communicated by A. S. Eddington, F.R.S.

XXIV. H. Dingle. "The Spectrum of Ionised Fluorine (F II)." Communicated by A. Fowler, F.R.S.

XXV. F. J. Wilkins and E. K. Rideal. "The Kinetics of the Oxidation of Copper.—I and II." Communicated by T. M. Lowry, F.R.S.

XXVI. C. P. Snow. "Infra-red Investigations of Molescular Structure.—V." Communicated by T. M. Lowry, F.R.S.

XXVII. J. Chadwick, F.R.S. "The Scattering of α-Particles in Helium."

XXVIII. H. Terrey. "A Note on the Supposed Dehydration of Hydrated Platin-Cyanides on Cooling." Communicated by F. G. Donnan, F.R.S.

XXIX. G. T. P. Tarrant. "The Absorption of Hard Monochromatic Rays." Communicated by Sir Ernest Rutherford, P.R.S.

XXX. E. J. Williams. "The passage of Slow β-Particles through Matter." Communicated by W. L. Bragg, F.R.S.

XXXI. P. E. Shaw and R. F. Hanstock. "Tribo-Electricity and Friction.—VI and VII." Communicated by Sir William Hardy, F.R.S.

XXXII. G. P. Thomson, F.R.S., and C. G. Fraser. "An Apparatus for Electron Diffraction." Communicated by Sir Joseph Thomson, F.R.S.

XXXIII. G. P. Thomson, F.R.S. "The Analysis of Surface Layers by Electron Diffraction." Communicated by Sir Joseph Thomson, F.R.S.

XXXIV. C. G. Lyons and E. K. Rideal. "On the Stability of Unimolecular Films.—IV." Communicated by Sir William Hardy, F.R.S.

XXXV. W. R. Andress. "A General Solution of Einstein's Equations for Systems involving Three Variables." Communicated by A. S. Eddington, F.R.S.

XXXVI. D. A. Jackson. "The Hyperfine Structure of the Arc Spectrum and the Nuclear Rotation of Indium." Communicated by F. A. Lindemann, F.R.S.

XXXVII. M. L. Chalk. "The Spectrum of H_2: the Bands ending in $2p'\pi$." Communicated by O. W. Richardson, F.R.S.

XXXVIII. A. F. Stevenson. "The Intensity of Quadripole Radiation in the Alkalies and the Occurrence of the Forbidden Line." Communicated by R. H. Fowler, F.R.S.

PROCEEDINGS OF
THE ROYAL SOCIETY.

Section A.—Mathematical and Physical Sciences.

A Comparative Study of the Excitation of Soft X-Rays from Single Crystal Surfaces and from Polycrystalline Surfaces of Graphite and Aluminium.

By O. W. Richardson, F.R.S., Yarrow Research Professor of the Royal Society, and Ursula Andrewes, Ph.D., King's College, London.

(Received March 1, 1930.)

A.—Graphite.*

1. *Introduction.*

These experiments originated in an attempt to improve and extend those of Richardson and Chalklin† on the soft X-rays generated by a tungsten surface deposited on carbon in a vacuum. The results obtained with the carbon alone, however, were so very much more complicated than those found by Richardson and Chalkin that an attempt had first to be made to arrive at some understanding of these results before the effect of depositing tungsten on the carbon could be investigated. The method consisted in bombarding the carbon target with electrons from a glowing filament and measuring the photoelectric current produced when the soft X-rays generated by this bombardment fell on a nickel plate. The photoelectric current per unit thermionic current is then plotted against the bombarding voltage as this is increased in small steps and discontinuous changes of slope in the resulting curves are observed.

2. *Apparatus and Method.*

The experimental tube was of quartz and similar in design to that used by Richardson and Chalklin. It was connected through three liquid air traps, one containing coconut charcoal, to a three-stage Gaede diffusion pump backed by a box oil pump and a Geryk oil pump. With this arrangement no difficulty was found in quickly obtaining and maintaining pressures which were certainly less than 10^{-6} mm. and probably of the order of 10^{-8} mm. The cylindrical shield, condenser plates, photoelectric plate and box were made of nickel and the cathode consisted of about three turns of 2 amp. tungsten wire. In Richardson and Chalklin's experiments a revolving type of target was used so that one face might be bombarded during the degassing process and the other used for the measurements, but it was found impossible to restrict the deposition of matter during bombardment to the side of the target facing the cathode and hence, in this apparatus, the target used was of another form in order to avoid this difficulty. The first type of target used is shown in fig. 1. It is made in two halves, one of which can be rotated, by means of an external magnet operating on the soft iron studs *a*, so that it completely covers the other half during the degassing bombardment. After this is complete the target is opened out and the experiments made on the clean inner surface. This target was made from gas carbon which, though rather brittle, is fairly hard. It was thought that some of the effects obtained with this target, although it was known to be fairly pure, might be due to impurities, so another target was made from spectroscopically pure carbon kindly supplied by Dr. R. C. Johnson. This carbon was so very much softer than the other that it was found impossible to make it in the previous hinged form and another device had to be adopted. This second target is shown in fig. 2. The whole tube was rotated through 90° so that the target arm was horizontal. The target was again made in two halves and one half could be slid over the other to cover it during the degassing process.

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* A preliminary account of some of the results of this section was published in a letter to 'Nature' of March 9, 1929.

† 'Roy. Soc. Proc.,' A, vol. 119, p. 71 (1928).

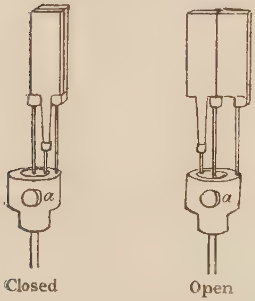

Fig. 1.

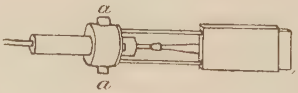

Fig. 2.

The tube and electrodes were degassed by heating with a blowpipe and the target was then maintained at red heat for several hours by electron bombardment until the pressure fell to about 3×10^{-5} mm. Even after this degassing it was found desirable to bombard the target for about half an hour at red heat every day before taking readings.

The electrical connections are shown in fig. 3.

The battery V_1 supplies the bombarding voltage between the filament, the negative end of which is earthed, and the target. This voltage is measured by the voltmeter V. The cylindrical shield is maintained at about 30 volts negative to the filament by means of the battery V_2, and V_3 supplies the potential difference of about 110 volts between the condenser plates. Preliminary tests were made and it was found that, with this arrangement, no positive ions or electrons were able to reach the photoelectric plate P. The photoelectric box B is kept at about 40 volts positive to earth by means of V_4. The plate P is connected to one pair of quadrants of a Dolezalek electrometer of sensitivity about 1250 mm. per volt and also to one end of the high resistance R. The other pair of quadrants is earthed and the high resistance is connected to a sensitive potentiometer by means of which it can be made slightly negative to earth. The high resistance used in nearly all the experiments was one made of glass containing cupric oxide and was of the order of 2×10^{11} ohms. Runs were usually made over a range of from 50 to 60 volts at a time in steps of 1 or 2 volts, and the bombarding current and potential on the high resistance were so arranged that the whole electrometer scale was used in

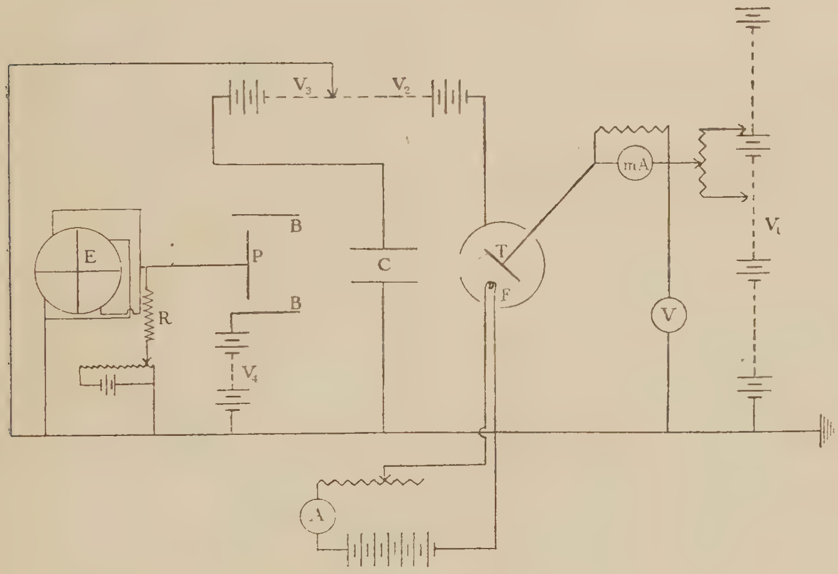

FIG. 3.

each run. It has been shown by Richardson and Chalklin that the total correction necessary to apply to the measured voltage is $+ 4 \cdot 9$ volts after allowance has been made for the voltage drop down the filament. This is the correction that has, therefore, been made in every case.

3. *Results and Discussion.*

The critical potentials found with the two carbon targets are collected in Table I. In one column are given the corrected values in volts and in the other the ratio of the number of times the particular discontinuity was obtained to the total number of curves taken over that range. This ratio, therefore, gives to some extent a measure of the intensity of the critical point.

It will be observed that, up to about 200 volts, there are many more values for the second target than for the first. This is partly because few curves were taken for the first target over this range and partly because these curves were taken at the beginning of the investigation when neither the precision of measurement nor the sensitivity were as good as later on in the experiments. Over the range from 200 to 375 volts, over which both targets were carefully examined, it is seen that there is very good agreement between the values found for both of them, and only in four cases are there breaks which were not found with both targets. From this it seems reasonable to conclude that very few, if any, of the critical values are due to impurities. The only likely impurities are tungsten, from the filament, and nickel, from the surrounding electrode, but as the targets were very carefully shielded, as explained above, both during the preliminary degassing of the tube and during the actual bombardment, it is very improbable that either metal could have been deposited on the target to more than a very small extent. Also, the targets were always removed from the tube and scraped after they had been in use a short time, as an extra precaution.

In two series of experiments with target I (series V and VI) after the clean inner surface had been examined over the range from 200 to 380 volts, it was heavily bombarded in an attempt to deposit tungsten on it and examined again over the same range. All the breaks found before the bombardment were repeated after it, the only differences being that those at 245 and 264 volts were more marked after the bombardment. In fact, that at 264 volts was absent before bombardment in series V. This rather supports the suggestion made by Richardson and Chalklin that these two critical potentials might be due to tungsten.

Table I.

Carbon target I.		Carbon target II.		Graphite target I.		Graphite target II.	
V.	*i.*	V.	*i.*	V.	*i.*	V.	*i.*
		23·2	3/3				
		27·8	2/3				
36·0	1/1	36·2	2/3				
		42·8	3/3				
53·8	2/2	53·0	2/3				
60·0	3/3	61·8	3/3			63·0	4/4
65·0	1/1	66·0	2/3				
						72·3	4/4
81·0	3/3	79·7	6/6	81·2	3/4		
		86·7	5/6			84·3	3/3
		90·9	6/9	92·0	4/5	91·6	1/3
		95·2	5/8			96·0	3/3
		100·7	7/9				
106·0	2/4	107·2	9/10				
		113·9	6/10				
116·0	2/3	116·1	2/11				
		120·2	5/10	123·0	4/5	122·3	3/3
125·5	2/3	126·0	5/8				
		130·6	3/9	129·7	3/4	130·0	3/4
		135·1	4/9				
142·5	2/2	141·0	5/8	140·7	3/4	140·4	3/4
		145·9	7/8				
		158·9	7/7	153·5	3/5	157·5	2/2
167·4	1/1	170·4	6/6	169	1/4	169·6	4/5
178·4	1/1	178·2	5/8	180·2	3/4	181·3	4/4
		183·9	3/8	187·5	2/5		
191·5	2/3	190·1	3/5	193·7	3/6	189·9	4/6
202·5	1/3	201·6	3/4	198·4	3/3	201	3/3
				206·2	2/3		
216·5	8/10	215·0	4/4				
				220·6	6/6	219·2	3/3
224·8	4/10	226·1	2/2	229·3	3/5	225	1/1
232·8	7/11	236·1	2/2				
240·8	4/9	241·0	1/2			240·5	1/2
245·9	9/12	244·4	3/3				
250·9	6/12	250·8	3/4	249·2	4/5	249	2/2
259·0	14/18	258·7	4/4			259	1/2
264·0	6/13						
269·2	7/14	268·4	5/5	267	4/4	267·1	2/2
		274	1/4	274·3	3/4	274·5	2/2
276·9	14/17					279·1	2/4
281·7	13/17	283·7	3/4	283	1/3		
288·6	11/16	288·3	3/3	289·5	4/4	289·3	4/4
294·3	10/14	293·7	3/3	296·5	4/4		
299·1	8/15	298·9	4/4			298·2	3/3
304·5	7/18	306·4	3/4	308·0	1/1		
311·1	11/18	310·0	1/3				
317·0	10/15	315·6	5/5				
325	11/16	325·2	2/2				
333	12/17	333·8	3/3				
		337·4	1/2				
340·7	11/19	340·7	2/2				
347·2	12/17	346·2	2/2				
356·3	5/10	357	1/2				
364·8	3/9	365·7	2/2				
372·5	10/10	372·1	2/4				

And the following values above 375 volts, which were measured on the pure carbon target (II) only, viz. :—377·6 (5/5), 388·3 (3/6), 381·1 (4/7), 392·4 (3/7), 398 (5/7), 403·3 (6/7), 409 (3/7), 413·2 (2/3), 421·5 (2/4), 425·3 (5/6), 432·1 (4/5), 438·3 (4/4), 445 (3/3), 454·5 (3/4), 465·7 (5/5), 471·8 (2/5), 478·5 (4/5), 485·9 (4/5), 495·7 (4/4), 501·5 (1/3), 507·0 (2/2), 513·3 (2/2), 519·6 (4/4), 526·5 (4/4), 536·4 (2/3), 545 (2/2), 556 (2/2).

It is clear from the experiments which have been described that there is a large number of discontinuous changes in the soft X-ray excitation from carbon which have nothing directly to do with processes equivalent to the displacement of electrons in atomic orbits. The discontinuities found are spread fairly uniformly, though without any obvious regularity, over the range from 20 to 560 volts. It should, however, be pointed out that most of these discontinuities are only to be found when electrical apparatus of high resolving power is employed. They make little or no impression on the general trend of the i_p/i_t : V curves when these are plotted over a wide range. They appear to be of the nature of small scale fluctuations superposed on a phenomenon of much larger magnitude. If, instead of making very precise measurements at points very close together over a small range of voltage, the points are widely separated over an extended voltage range, the character of the curves is similar to that of those already published by Richardson and Chalklin.* In these the main changes in the general trend of the curves take place at, or near, voltages corresponding to the Bohr levels.* At the same time, if the phenomena are examined over a small range of potential only, the numerous discontinuities here recorded look as definite and pronounced as those which are able to make their effects felt over a wider range.

We have devoted a good deal of consideration to the question of the origin of all these discontinuities which is very puzzling. It would, no doubt, be very convenient if they could just be dismissed as illusory, arising from faults in the experimental method. The results, however, show too much consistency for this explanation to be probable. Many of the inflections appear time after time within a fraction of a volt of the same place. Possibilities which might give rise to a distribution of discontinuities of the type found are: (1) Electron jumps to virtual orbits of the type with which Richardson and Chalklin have had a certain amount of success in reducing the complicated phenomena shown by the metals with atomic number in the neighbourhood of 26. We have tried this method but the results have not been satisfactory. It is also rather dangerous as it gives formulæ well adapted for representing a set of numbers which are spread irregularly but with some uniformity over a given range of values. (2) Vibration bands of the electrons in the solid. A fair representation of a considerable part of the data could be got by this method but the inflections are so confused that this might have been the result of accidental coincidences. (3) Effects due to electron reflection, electron waves and secondary electron emission. These might operate in various ways which we shall not take the time to discuss here.

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* These statements apply only to polycrystalline specimens. The curves got with single crystals have a different appearance and will be dealt with in a later paper.

4. *Experiments with Natural Graphite.*

With a view to reducing the number of variables involved in the experiments we resolved to investigate the behaviour of single crystal faces with respect to these phenomena. Prof. W. T. Gordon of the Geology Department of King's College, kindly furnished us with a diamond with a large natural face and also some large crystals of natural graphite and of iron. We tested the electrical conductivity of the diamond and found it to be zero so far as we could ascertain ; so that diamond does not seem to be a suitable material for experiments of this kind. The iron crystals also did not seem to be very satisfactory, owing to irregularities in them.

After some trials we were able to split off a piece of the crystalline graphite with a surface large enough to be suitable for testing. The surface used was that at which natural graphite cleaves most easily (the 0001 plane). It was not possible to use any protective cover for this target during the bombardment so the target was made of the rotating type. It was rather small and was mounted in a nickel clamp. The slit in the guard cylinder was made much shorter so as to ensure that no radiation from the nickel holder should reach the photoelectric plate. Two pieces of graphite were used in turn so that the results from one might be checked by the other. Both had plane faces which were cleavage faces but the faces were by no means composed of only one crystal. It seems that graphite forms in rather small crystals, and it is difficult to obtain a single crystal of any considerable size.

The critical potentials found with the natural graphite targets are given in the last two columns of Table I. It is seen, first of all, that there are not so many critical points found as for the ordinary carbon target (II) in the range examined, which extended from 50 to 310 volts. There are only two points which are quite new, namely, 70·3 and 206·2 volts, and one belongs to each target. There are 14 points found with both targets and with the possible exception of four they were all found with the carbon targets. The element of doubt about the four arises from the fact that some of them are weak inflexions and difficult to locate with sufficient accuracy to make the identifications certain.

These results certainly indicate that the simpler the crystal structure of the surface, the fewer are the number of the critical potentials likely to be found. They also confirm the conclusion that there are a large number of critical potentials which have little or nothing to do with the Bohr levels.

Although the numbers in Table I look very irregular, they can be arranged according to a regular numerical scheme. We consider first of all the data given in the last column as being the most complete of the two graphite crystal targets and likely to be simpler than those for the pure carbon target (II). Nearly all of these are included in Table II.

Table II.

Critical potential	240·5		249·1		259		267·1		274·1		279·1
Horizontal difference		8·6		9·9		8·1		7·3		4·7	
Vertical difference	59·7		57·6		59·3						
Critical potential	180·8		191·5		(199·7)						
Horizontal difference		10·7		8·2							
Vertical difference	58·1		61·6		59·1						
Critical potential	122·7		129·9		140·6						
Horizontal difference		7·2		10·7							
Vertical difference	59·7		57·6		56·3						
Critical potential	63·0		72·3		84·3		91·9		96·0		
Horizontal difference		9·3		12·0		7·6		4·1			

Table III.

Critical potential	(199·7)		216·0		233·4						
Horizontal difference		16·3		17·4							
Vertical difference	44·2		46·5		45·9						
Critical potential	155·5		169·5		187·5		206·2		220·1		227·2
Horizontal difference		14·0		18·2		18·7		13·9		7·1	
Vertical difference	50·6		49·1		52·4		60·3 (?)				
Critical potential	106·9		120·2		135·1		145·9 (?)				
Horizontal difference		13·3		14·9		10·8?					

Table IV.

Critical potential	100·7		113·9		125·9
Horizontal difference		13·2		12·0	
Vertical difference	47·3		48·2		45·5
Critical potential	53·4		65·7		80·4
Horizontal difference		12·3		14·7	

It will be seen that the numbers in Table II have the same type of numerical relationship as that of the frequencies of the lines in a set of bands. As a matter of fact Table II includes all the critical potentials of the crystal target II except six and these include the two near 290 which belong to or are mixed up with the carbon K inflection. If these are added to the remaining discontinuities got from crystal target I (3rd V column of Table I) and the values for the two close pairs of which only one is found on each target are averaged, then all the values except those mixed up with the K inflection form a single band-like sequence with somewhat wider spacing, namely, 155·5, 169·3, 187·5, 206·2, 219·9 and 227·2. These have the successive differences 13·8, 18·2, 18·7, 13·7 and 7·3.

It now appears that if this sequence is added to the numbers given by the pure carbon target II (2nd V column of Table I), which are *not* found with either crystalline target, these numbers can be arranged in another scheme, or rather two schemes, similar to Table II. These are set out in Tables III and IV. In Table II the mean values got from the two crystals are used, and in Tables III and IV the means of the remaining values. The position of 145·9 and of 199·7 is doubtful.

These schemes take in all the critical potentials in the gap between the carbon K and L regions given in Table I except 245·1 and 264·0. It is significant that these two breaks are identical with tungsten values.* 145·9 is also close to one of the sputtered carbon values (142·6) given by Richardson and Chalklin.

It is obvious that a metal is a structure which has parts capable of vibrating under electronic excitation and the voltage differences found are of the right order of magnitude for such effects.† We do not, however, wish to enter into theoretical details until we have some more experimental evidence, particularly as something like the observed data could be simulated by electron wave phenomena.

B.—ALUMINIUM.

First of all a pure aluminium target with a pure aluminium cover was used and tested for breaks over the range 0–150 volts. The cover alone was bombarded. The following breaks were obtained: 27·9 (2/3), 40·4 (3/3), 53·2 (3/3), 58 (1/4), 61·3 (6/7), 71·6 (6/7), 79·4 (6/7), 85·6 (5/7), 92·5 (4/5), 98·9 (4/4), 111·1 (3/3), 122·6 (2/2), 130·1 (2/2), 137·5 (1/2), 142·7 (2/2).

A large crystal of aluminium was very kindly supplied to us by Mrs. Tipper (Dr. C. F. Elam). This was carefully cut without damaging the crystal structure so as to form a target having as its front face one of the faces‡ of the crystal.

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* Richardson and Chalklin, *loc. cit.*

† A fuller treatment of this point of view will be given in a paper now in course of preparation by one of us (O.W.R.).

‡ This description requires modification. Since these experiments were made the aluminium crystal used has been very kindly examined for us by Miss E. Knaggs on an X-ray spectrometer at the Royal Institution. She found that the polished face of the

This was then tested in the same manner as the polycrystalline specimen and using the same cover. The following critical values were obtained : 41·9 (2/2), 53·7 (3/3), (?) 57·2 (2/2), 63·2 (3/5), 66·7 (1/3), 108 (1/1), 115·2 (1/1), 121·5 (1/1), 130·3 (2/2), 139·4 (1/1), 144·2 (1/1).

The range between 67 and 107 volts was gone over carefully twice but no discontinuities were found in it. It will be seen that, with the exception of the two discontinuities measured at 66·7 and 115·2, all the values found with the crystal can be identified with values given by the polycrystalline aluminium. On the other hand, the string of values 71·6, 79·4, 85·6, 92·5 and 98·9 which are very evident on the polycrystalline specimen are quite absent with the crystal. This is quite similar to the case of graphite where the values which are absent on the crystal tend to run together.

The values given by the crystal fall into two groups with a similar arithmetical structure to that of those given by the graphite data. This is shown in Table V where all the inflexions given by the crystal are used except the doubtful weak inflexion at 57–58 and the one at 115·2 which was only observed once. As this is not confirmed by the observations on the polycrystalline specimen it may well be an accident. We have added the value at 27·9 to the crystal values. There is an inflexion in this neighbourhood on the crystal curves but the currents are too small to locate it with precision.

As is shown in Table VI the remaining values not given by the crystal seem to conform to a similar structure. This Table uses all the remaining values.

Table V.

Critical voltage	109·5		121·5		130·3		139·4		144·2
Horizontal difference		12·0		8·8		9·1		4·8	
Vertical difference	81·6		80·3		76·8		77·1		
Critical voltage	27·9		41·2		53·5		62·3		
Horizontal difference		13·3		12·3		8·8		4·4	

Table VI.

Critical voltage	79·4		92·5		
Horizontal difference		13·1			
Vertical difference	7·8		6·9		
Critical voltage	71·6		85·6		98·9
Horizontal difference		14·0		13·3	

target did not coincide with any important crystal plane or face. The nearest one to it (of reasonably large spacing) was the (200) plane. There was a very small portion of a different crystal in the centre of the target, forming about 2 per cent. of the whole surface. But the (200) planes of the main crystal and the small part make nearly the same angles with the target surface, *i.e.*, 9° and 8½° as seen from the top of the specimen and — 22½° and — 23° as seen from the side.

In the foregoing experiments with the crystal it was observed that the value of i_p for the crystal was always very much higher than that for the cover at the same heating current, although, owing to the greater distance between the filament and the target, the thermionic current i_t was slightly less for the crystal. A few curves were therefore taken over a range of about 700 volts with the crystal and the cover in turn. They were found to be very different, the value of i_p/i_t being much greater for the crystal at voltages up to 400–500 volts. In this region the curves crossed and the values for the cover became greater. The results of a typical experiment are shown in fig. 4, in which the points given by the crystal are shown thus : ⊙ and those given by the cover ×.

In order to ascertain whether the difference in the curves was due to the crystalline state of one target or to some other cause, such as oxidation of the cover or deposition of foreign matter upon it, the original target and cover of pure aluminium were remounted in the tube and tested in a similar way over the range up to 600 volts. At first the cover alone was bombarded ; the curves were quite different from those obtained with the crystal and cover and were also different from each other. The value of i_p/i_t was much greater for the

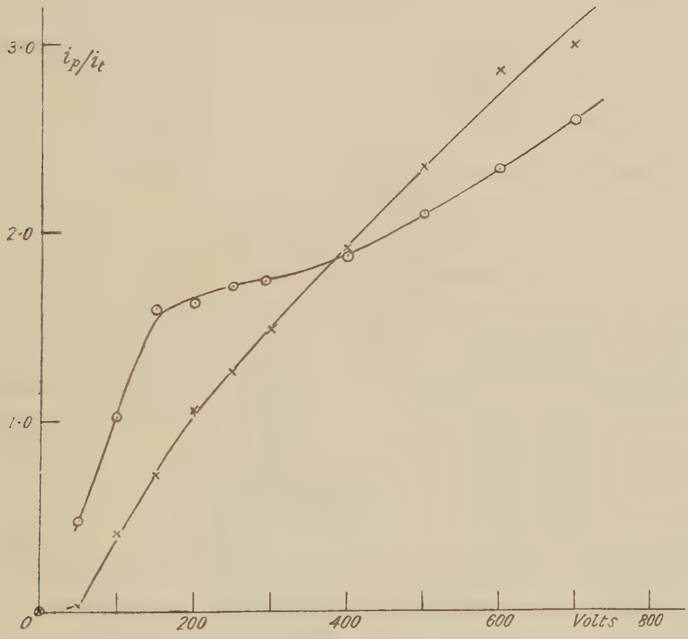

Fig. 4.

target than for the cover right up to 600 volts but the general shape of the curves was the same and they showed no tendency to cross over. The target was then bombarded for 20 minutes with the result that the values of i_p/i_t for it became smaller and the two curves approached one another. Further bombarding of the target ultimately made the two curves practically identical.

The cover was then bombarded in hydrogen with the result that the curve for the cover became slightly higher. The target was then subjected to the hydrogen treatment, and finally, after both had been bombarded in hydrogen for 1 hour, identical curves were obtained.

Two curves were then obtained at small voltage intervals to test for breaks and almost the same breaks were found with the cover and the target, viz. : -

Table VII.

Original values	41·2		53·5	57·6*	62·5	66·7†	71·6‡	79·4‡
Cover		45·5		59·5		68·2		78·5
Target		45·0		57·0		67·5		76·5
R. and C.§		45·6		54·0		70·4		75·6

* Very weak. † Crystal only. ‡ Polycrystalline target only.

This sequence of breaks is not the same as that got originally from the target and crystal, but they are similar to the sequence got by Richardson and Chalklin§ for a carbon target bombarded with a tungsten cathode. Any differences may be due partly to errors and partly to the effect of substituting carbon for aluminium as the support. The very pronounced inflexion at 45·5 volts shows clearly that, at this stage, the cover had the properties of a contaminated cathode. This would account for the smaller currents given by it at the lower voltages. It will not account for the flattening out of the curve for the crystal at high voltages. This feature is not shown by the clean polycrystalline aluminium and must be a specific property of the crystal surface.*

In the last experiments the efficiency of the polycrystalline target before it had been subjected to direct bombardment was two to three times that of the cover, the precise ratio being a function of the voltage up to 600 volts. Bombarding the cover with the target underneath does not affect this ratio much, but direct bombardment of the target with the cover removed causes its efficiency to drop rapidly towards equality with that of the cover. This drop is due to contamination during bombardment as is shown by the change in the discontinuities from the aluminium values to values near those given by a carbon target contaminated by bombarding. It is not likely to be due to oxidation because heating in hydrogen, either of the target or the cover, only produces relatively small effects. However, it was not possible to heat to very high temperatures so that this may not have been an efficient reducing agent. In any event there is no evidence of oxidation.

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* Since this paper was written we have made similar tests with the graphite crystal surface, and this shows a similar flattening out at the higher voltages when compared with the polycrystalline specimen.

§ 'Roy. Soc. Proc.,' A, vol. 119, p. 78 (1928).

A similar series of observations was now made with the crystal target. It was first cleaned by scraping very gently with a razor blade and then remounted with the same cover as before. The results of this set of experiments are shown in fig. 5, in which values of i_p/i_t given by the cover are indicated thus × and those given by the crystal thus ⊙. The range of observations is from 0 to 600 volts in each case. The curves are on the same scale but are displaced along the voltage axis to avoid confusion. After the cover had been bombarded for 3 hours, with the crystal behind it, curves 1 and 2 were obtained. The crystal curve 2 is not of the same type as that previously obtained (fig. 4), but

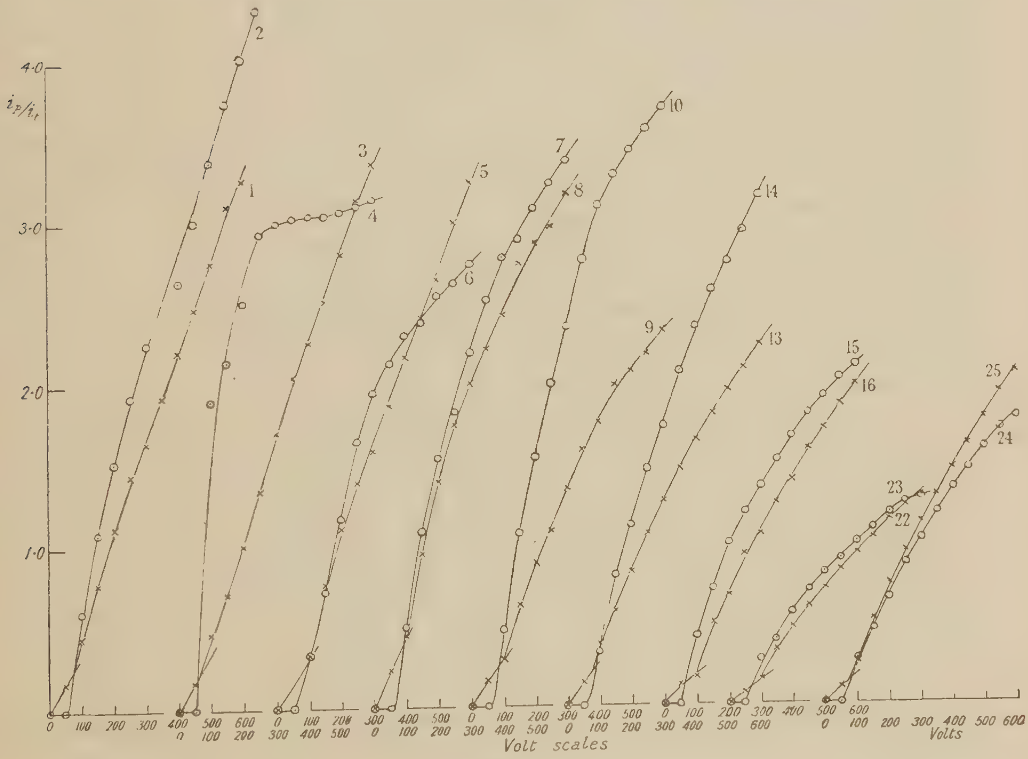

FIG. 5.

it should be remarked that during this particular set of observations the tube appeared to be insufficiently baked out for satisfactory working. The thermionic current was unstable and increased continuously during the course of the experiments. At the same time this does not seem to us to be an adequate explanation of a radical change in the shape of the curve. In fact we do not know what this particular set of observations means but we think it should be recorded. After the cover had been bombarded in a similar way for 8 hours altogether we obtained curves 3 and 4. These are of the type got before and show a well-marked saturation effect with the crystal at about 250 volts. When the cover had been bombarded for 11 hours altogether curves 5 and 6 were obtained. This shows a less well-marked saturation in the crystal curve. Up to the beginning of this experiment the thermionic current had only been playing on to the crystal for 35 minutes altogether. Without further bombardment, but after the thermionic current had been allowed to run on to the crystal for an hour longer, curves 7 and 8 were obtained. The crystal is now showing the type of response characteristic of the polycrystalline metal and it remained in this condition throughout the rest of the experiments. It seems that this change from the flat type of curve got only with the crystal surface to that which is characteristic of the polycrystalline target and the cover can be brought about either by bombarding the cover or by allowing a thermionic current to flow into the crystal (unless the change is started by the bombardment and then goes on slowly by itself). After the cover had been bombarded for 12 hours, curves 9 and 10 were obtained. These are quite similar to those given in the preceding set of experiments with the polycrystalline target before the target had been bombarded. Several sets of observations similar to these were taken at this stage. After the cover had been bombarded for 12¼ hours altogether, curves 13 and 14 were got. The crystal was then bombarded for 20 minutes. The effect of this has been to bring the values for the crystal nearly down to those for the cover, as is seen from curves 15 and 16. After taking several similar sets of observations to these the cover was bombarded in hydrogen for half an hour and curves 22 and 23 were obtained. The crystal was then bombarded in hydrogen for half an hour and curves 24 and 25 were taken. It will be seen that there is now little difference between the curves.

After these observations a few short range curves were taken to test the breaks. The values measured were found to be as follows :—

Original values	27·9		41·2		53·5	57·6*	66·7†	71·6‡	79·4‡	85·6‡	92·5‡	98·9‡		109·6	122·1
Cover		39		46		57		69 ?	80						
Crystal		37 ?		46		57		71	82	87	94	98	105		120
R. and C.		37·4		45·6		54		70·4	81·5		91·4		105·5		

* Very weak. † Crystal only. ‡ Polycrystalline target only.

Only one curve was taken with the crystal above 82 volts, and the cover was not examined at all in this range. There are four curves for the lower range with the crystal.

These values are evidently not the same as those originally given by the crystalline target. In fact they are a mixture of the polycrystalline target breaks and those due to a cathode contaminated by sputtering from a tungsten filament. Most of the original polycrystalline breaks are now present, but in the lower range they have been swamped by the strong tungsten effects at 37·4 and 45·6 volts and the tungsten break at 105·5 volts has also appeared. The tube was now opened up and there was some slight evidence of contamination on the crystal. It was also submitted to Mrs. Tipper who informed us that the surface had recrystallised. These observations are in agreement with the conclusions drawn from the inflexions.

We conclude that when the crystal is giving the inflexion values found with it initially, the characteristic i_p/i_t against voltage curve flattens out at about 250 volts and that the subsequent changes are due partly to superficial recrystallisation caused by heating and by electron impact and partly to contamination due to deposition during bombardment.

The very pronounced feet of the crystal curves in fig. 5 is a mysterious feature of which we have no satisfactory explanation to offer. However, in the earlier experiments illustrated by fig. 4, the foot seemed to be on the curves for the cover, not for the crystal, so that this may not be a matter of much significance. It will be noticed that practically all the long-range curves show a pronounced bend somewhere between 50 and 100 volts. It is in this region that the Bohr L levels lie for aluminium. The somewhat higher value for the bend for the curves for the cover may be influenced by the deposit of tungsten and possibly other elements. A similar feature to this on the large-scale curves was noted with polycrystalline carbon.

In conclusion, we wish to express our thanks both to Prof. Gordon, for providing us with a number of crystal specimens, and to Mrs. Tipper, who not only supplied us with the aluminium crystal but also very kindly placed her valuable experience at our disposal.

The Excitation of Soft X-Rays from some Polycrystalline Metal Surfaces.

By O. W. Richardson, F.R.S., Yarrow Research Professor of the Royal Society, and S. Ramachandra Rao, M.A., King's College, London.

(Received March 1, 1930.)

§ 1. *Apparatus and Method.*

This investigation is a continuation of the work of Richardson and Chalklin* using similar experimental methods. The metals investigated are nickel. cobalt, copper and tungsten. The first part of the investigation consisted in the determination of discontinuities in the curves obtained when the X-ray yield (i_p/i_t) is plotted against the exciting voltage, with the object of extending the tables published by Thomas, Compton and Thomas, Richardson and Chalklin, Davies and Horton, and Andrewes, Davies and Horton,† and of ascertaining the consistency of these inflexions under different conditions. One result has been to confirm the reality of the inflexions. On the other hand the number of them has increased to a degree that is bewildering, so that the interpretation that should be put upon them is still not certain. It should perhaps be pointed out that a series of points such as those given by the experiments to be described can be connected in various ways so as to exhibit discontinuities at various places. Ours have all been drawn so that the discontinuities represent sudden increases in i_p/i_t in the manner shown by figs. 2, 3, 8, 9 and 10.

The targets used as anticathodes were rectangular plates of metal, 2 cm. by 1 cm. by 1 mm. In the case of cobalt the plate was rigidly fixed to a thin nickel rod at the back and mounted inside the tube as usual. The copper target and the supporting rod were cut from the same piece, while nickel and tungsten were fixed on nickel rods. The targets could be rotated by a magnetic device in the manner adopted by Richardson and Chalklin.

Having obtained an initial pressure of 10^{-6} mm., the tube was thoroughly heated, the filaments glowed for a long time and subsequently the target heated by electronic bombardment to bright redness. This operation was continued until there was no more evolution of gas from the metal parts. During the process of heating the target by electronic bombardment, the back face of the target was directed towards the filament and the fresh front face was brought round only when the readings were taken. The targets were taken down after about 10 hours of work on the front surface, cleaned and set up again, thus ensuring a pure and clean face during the observations.

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* 'Roy. Soc. Proc.,' A, vol. 110, p. 247 (1926), vol. 119, p. 60 (1928), and vol. 121, p. 218 (1928).

† Thomas, 'Phys. Rev.,' vol. 25, p. 322 (1925); Compton and Thomas, 'Phys. Rev.,' vol. 28, p. 601 (1926); Richardson and Chalklin, *loc. cit.*; Davies and Horton, 'Phil. Mag.,' vol. 2, p. 1253 (1926); Andrewes, Davies and Horton, 'Phil. Mag.,' vol. 46, p. 721 (1923), 'Roy. Soc. Proc.,' A, vol. 110, p. 64 (1926), and vol. 117, p. 649 (1928).

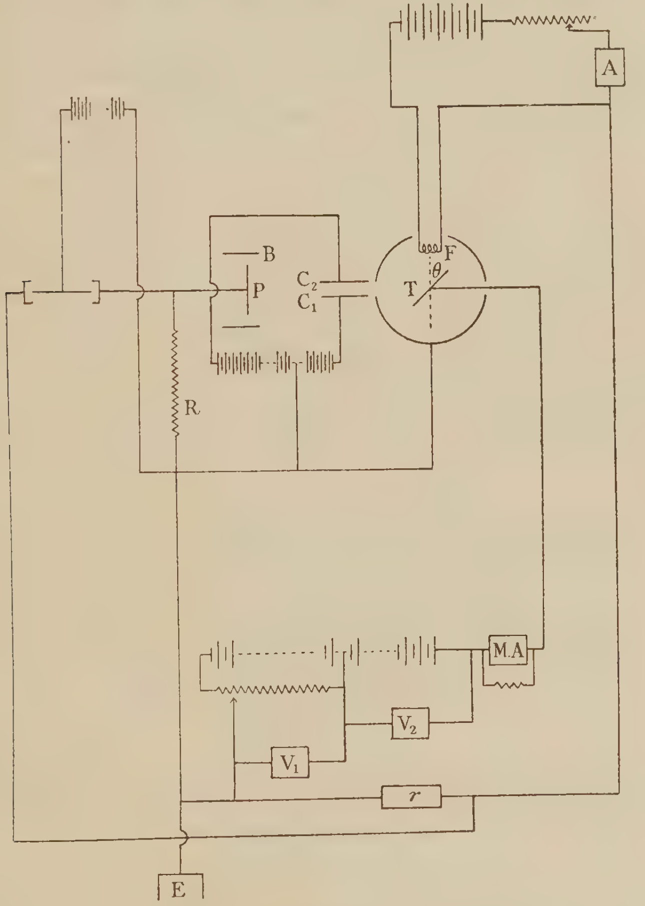

FIG. 1.—Soft X-Ray Electrical Connections.

The essential details of the apparatus and the electrical connections are shown in fig. 1. The cathode consisted of three turns of 2 ampere tungsten wire (F), and was glowed to a temperature of about 1800° to 2000° C. The liberated electrons were drawn to the target by the application of a positive potential. A part of the radiation so generated passed through two condenser plates, C_1 and C_2, maintained at potentials − 250 and + 50 volts, which were found to be more than sufficient to filter off the ions and electrons diffusing out of the X-ray tube. The filtered radiation was then incident on a photo-electric plate P of copper surrounded by a copper box B at + 50 volts. P was connected to one pair of quadrants of a Dolezalek electrometer of sensitivity 750 mm. per volt, and was also connected to one terminal of a high resistance R, the other end of which was earthed. This high resistance (nearly $2 \cdot 1 \times 10^{11}$ ohms) was similar to the one used by Richardson and Chalklin in their later experiments and was made by depositing lamp-black on a quartz rod.

The thermionic current was read by a milliammeter which was carefully calibrated with suitable standard resistances and which was shunted with a small resistance box. The negative end of a resistance r included in the thermionic current circuit was earthed while the positive end was connected to the other pair of quadrants of the electrometer. The voltages employed were supplied by storage cells and were applied in two segments V_1 and V_2, one segment V_2 being kept fixed and the other V_1 being varied usually from 0 to 60 volts. A Weston D.C. voltmeter reading to 1 volt was used at first, but in later experiments another Weston voltmeter with multiple ranges and 750 divisions on the scale was employed. With this precision voltmeter, voltages could be read accurately to one-tenth of a volt at potentials less than 150 volts.

If i_p and i_t are the photo-electric and thermionic currents in any experiment and R and r are the high resistance and the resistance plugged out in the box r respectively, it is seen that the opposing pairs of quadrants are charged to potentials $i_p R$ and $i_t r$. There will be no deflection if $i_p R = i_t r$. If, however, a deflection d is obtained, it will be given by the relation

$$i_p R - i_t r = kd, \tag{1}$$

where k is the electrometer constant. We obtain from this the following relation :—

$$i_p / i_t = r/R + kd/Ri_t. \tag{2}$$

The following method was adopted. When a range, say 300 to 360 volts was to be investigated, the resistance r was adjusted so that the deflection of the electrometer was nearly zero when the applied potential was about 330 volts. On increasing the potential gradually from 300 to 360 volts, the spot of light moved from one side of the scale to the other. The readings of the scale were taken every time the potential was increased by a definite amount. The value of the thermionic current was also noted at every potential.

This value of i_t remained nearly constant at potentials above 200 volts. If, therefore, at values higher than 200 volts, graphs are drawn between the applied potential and the deflection, the discontinuities will give the soft X-ray inflections. At potentials lower than 200 volts, the deflections were always divided by the corresponding values of i_t and the graphs were drawn between the applied potential and d/i_t. Thomas (*loc. cit.*) has taken half-volt intervals at low voltages. It is found with this method that 1-volt steps up to 200 volts, $1\frac{1}{2}$-volt steps up to 350 volts, and 2-volt steps above 350 volts are enough to fix the inflections. To bring out the inflections more clearly, i_p/i_t was plotted, as far as possible on a larger scale relatively to the voltage axis. Small changes in the slope are thus neatly shown, as will be seen from some of the curves reproduced in figs. 2 and 3.

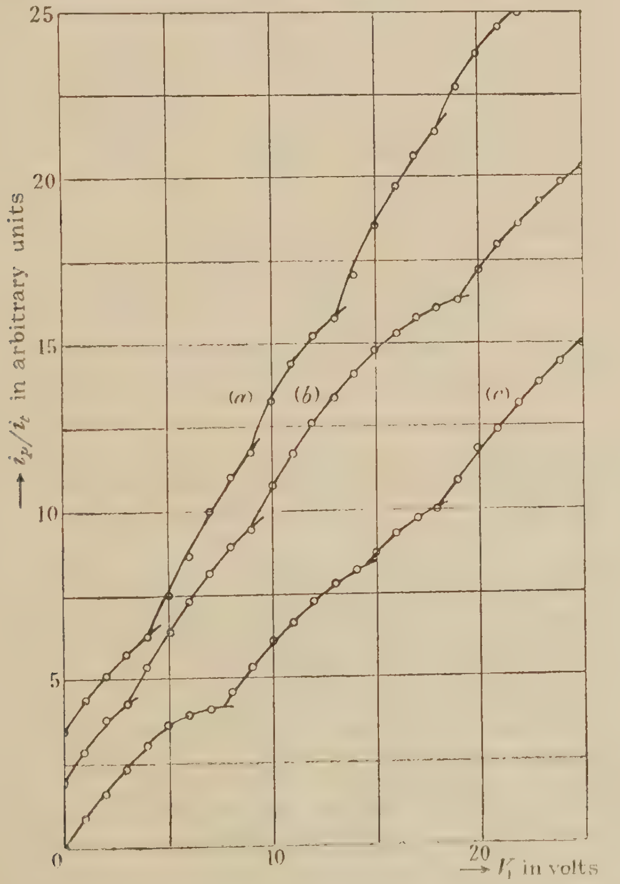

FIG. 2.—i_p/i_t curves for tungsten. (*a*) V_2 = 103·4 volts. (*b*) V_2 = 209·8 volts. (*c*) V_2 = 364·0 volts. The ordinates are entirely arbitrary. The applied potentials are uncorrected.

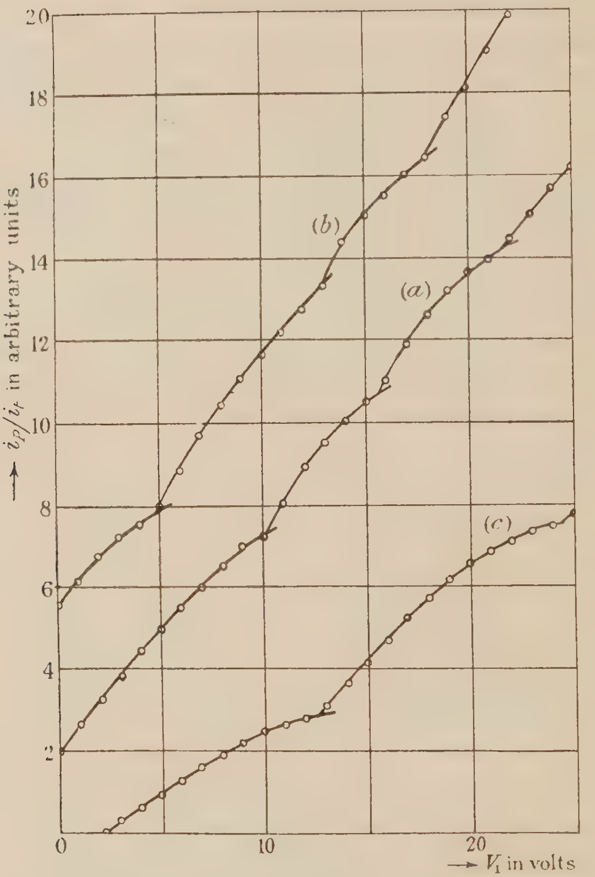

Fig. 3.—i_p/i_t curves for copper. (a) $V_2 = 111\cdot0$ volts. (b) $V_2 = 286\cdot0$ volts. (c) $V_2 = 466\cdot0$ volts. The applied potentials are uncorrected. The ordinates are entirely arbitrary.

The advantages of this method are clear. A large deflection of several hundred centimetres is balanced and the readings of the spot of light, which was always steady and perfectly focussed when they were taken, are very reliable. The method is a direct determination of the ratio i_p/i_t.

When the thermionic current varies very little with the driving voltage, *i.e.*, at potentials greater than about 200 volts, this method is very advantageous as it gives a direct method of studying the variation of i_p/i_t and eliminates the use of auxiliary cells and resistances. But at lower voltages, where the thermionic current affects the sensitiveness of the method, there is a disadvantage. For, in the equation (1), both i_pR and i_tr decrease when the thermionic current is decreased, thus giving a smaller value for d. Here the method of Compton and Thomas is really advantageous since they do not use the thermionic current circuit to balance the photo-electric potential i_pR. In these experiments, however, this point did not give any trouble, since up to nearly 150 volts, r was zero and between 150 and 200 volts the sensitivity was not greatly affected, since r was made as small as possible.

Corrections.—The corrections that should be applied to the readings of the voltmeter have been considered at some length by Richardson and Chalklin in their first paper (*loc. cit.*). In this paper their value of $+ 4 \cdot 9$ volts has been taken as the work necessary to drag an electron out of the hot cathode. Besides this correction for the work function we have to consider the potential drop across the filament. Taking the middle third of the filament as the hottest and the most effective in the liberation of electrons, the correction would be to subtract one-third of the drop in potential along the filament from the readings of the voltmeter. This is because the voltmeter was connected to the negative end of the filament. Further, there is the fall of potential across the resistance r. This value of $i_t r$ must be subtracted from the voltmeter readings. For each set of values, the total correction was calculated and applied to the readings of the voltmeter. The results given in the following tables are all corrected in this manner.

§ 2. *Critical Potentials of Cobalt.*

In the case of cobalt, measurements have been made from 210 volts to 1050 volts. The results are given in Table I. The values obtained by Thomas are also given for comparison.

In this and similar tables the first figures in brackets after our values are the intensities as estimated by eye from the apparent change in slope and are the averages from a large number of inflections in each case. All the changes in slope are upwards; the numbers are not *measurements*, and are only intended to give some idea of the comparative obviousness of the breaks. The fraction in the second bracket gives the proportion of the number of curves on which the inflection was found to the total number taken.

It will be seen that in the region from 210 to 335 volts, the values are in good agreement with those of Thomas. Some new inflections have been detected, namely those at 235·2, 271·8 and 317·9 volts. Between 343·8 and 700 volts, as many as 35 inflections have been noted, none of which appeared in the work of Thomas. Above 700 volts the agreement is poor. Whereas inflections have been obtained here at 775·0, 836·5, 856·5 and 900·6 volts, Thomas has recorded values at 705·2, 764·8, 873·2 and 950·1 volts. This

Table I.—Critical Potentials of Cobalt.

Authors	214·6 (1·1) (8/8)	224·2 (0·9) (7/8)	230·5 (1·1) (7/8)	235·2 (0·3) (2/8)
Thomas	214·0 (1·3)	223·0 (1·4)	230·8 (1·9)	
Authors	243·8 (0·8) (6/8)	253·1 (1·2) (8/8)	264·5 (1·3) (7/7)	271·8 (0·2) (2/7)
Thomas	244·8 (1·1)	255·5 (1·5)	264·6 (1·3)	
Authors	276·3 (0·8) (7/7)	284·7 (0·8) (7/7)	292·0 ? (0·8) (7/7)	304·6 (1·0) (7/7)
Thomas	277·4 (1·8)	285·1 (1·5)	293·7 (1·2)	306·5 (2·1)
Authors	317·9 (0·7) (7/7)	326·9 (0·7) (6/7)	335·0 (0·6) (6/7)	343·8 (0·8) (7/7)
Thomas		326·3 (1·2)	335·8 (2·3)	
Authors	354·6 (0·9) (7/7)	369·0 (1·0) (8/8)	380·0 (1·0) (7/8)	388·0 (0·8) (7/8)
Authors	400·0 (0·9) (11/13)	418·0 (1·5) (5/5)	431·7 (1·2) (10/10)	436·5 (1·4) (5/5)
Authors	442·0 (1·1) (5/5)	446·3 (0·5) (3/5)	450·0 (1·0) (4/5)	456·3 (1·2) (5/5)
Authors	467·1 (2·1) (4/4)	483·5 (1·1) (4/4)	492·6 (0·8) (4/4)	505·2 (2·0) (5/5)
Authors	510·5 (1·5) (6/6)	516·4 (1·5) (6/6)	526·5 (1·6) (5/6)	536·5 (0·6) (5/6)
Authors	548·0 (0·8) (4/5)	556·8 (1·0) (3/3)	568·3 (0·9) (7/8)	575·3 (0·8) (5/8)
Authors	580·9 (0·7) (5/7)	586·3 (1·1) (6/7)	593·0 (0·8) (4/7)	599·0 (1·4) (5/5)
Authors	606·2 (0·8) (4/5)	612·0 (0·8) (2/5)	619·6 (0·9) (4/5)	628·6 (1·1) (4/4)
Authors	647·0 (0·5) (4/4)	—	775·0 (1·7) (4/4)	836·5 (0·9) (4/4)
Thomas	—	705·2 (1·1)	764·8 (1·8)	—
Authors	856·5 (1·3) (4/4)	—	900·6 (1·5) (3/3)	—
Thomas	—	873·2 (2·0)	—	950·1 (1·3)

range has been repeated several times very carefully and the same values have been obtained. This region is not crowded with values and it is worth while considering the energy of the L levels for cobalt in this connection.

As has been pointed out by Richardson and Chalklin in their third paper, these values may be associated with transitions between the L and M orbits of the cobalt atom. The X-ray values can be obtained from the emission measurements of Thoraeus.* These measurements give the values of the L_{II}, L_{III} and M levels. The value of the L_I level can be calculated since $L_I - M_{II\ III} = L_{\beta 3,\ 4}$ but Thoraeus' values of the $L_{\beta 3,\ 4}$ lines do not include cobalt. Stoner† has, however, calculated the energy of the L_I level from Sommerfeld's equation $(L_I)^{\frac{1}{2}} - (L_{II})^{\frac{1}{2}} = 0\cdot57$. Accordingly the values of the L and M levels can be found. The inflection at 900·6 can be associated with the removal of an electron from the L_I orbit outside the atom altogether or to the $M_{IV\ V}$ level. Stoner's calculated values for these are 917 and 907 volts. The line at 856·5 volts is probably due to the transition from the L_I to the $M_{II\ III}$ level, the calculated value being 852·9 volts. The value at 775 volts may be due to an electron being removed from the L_{III} orbit outside the atom altogether or to the $M_{IV\ V}$ level, the calculated values being 783·6 and 775·5 volts. There is besides an inflection at 836·5 volts. It is difficult to say exactly what accounts for this, but it is not improbable that it is due to multiple impact, that is, a bombarding electron removing at the same time one electron from the L_{III} level to the $M_{IV\ V}$ level, and another, in the same atom or in another atom, from the $M_{II\ III}$ level to the periphery. The total value in this case is 839·6 volts. Multiple impacts, especially of this double type, in such experiments as these, are by no means impossible. An electron may have sufficient energy after a resonance encounter to produce ionisation or resonance in another atom, as has been mentioned by Stoner (*loc. cit.*) in his discussion on the theory of Thomas on multiple impacts. The probability of such collisions should be small, and hence one should expect the intensity of such inflections to be small. The intensity of the break at 836·5 is seen to be much less than the intensities of neighbouring breaks, thus lending considerable weight to this view.*

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* 'Phil. Mag.,' vol. 1, p. 312 (1926).

† 'Phil. Mag.,' vol. 2, p. 97 (1926).

§ 3. *Critical Potentials of Nickel.*

Investigations have been made with this metal in the range from 300 to 565 volts. As in the case of cobalt, many inflections have been obtained, as many as 38 within this range. The values are given in Table II below.

Table II.—Critical Potentials of Nickel.

Volts (intensity).			
308·8 (0·6) (10/11)	315·5 (0·6) (11/11)	321·8 (0·5) (8/11)	327·1 (0·4) (6/11)
331·5 (0·5) (7/11)	337·6 (0·5) (11/11)	343·4 (0·3) (8/11)	349·8 (0·6) (10/11)
358·1 (0·3) (6/11)	361·6 (0·4) (2/3)	365·2 (0·3) (5/10)	369·7 (0·5) (5/7)
376·2 (0·5) (6/7)	384·6 ? (0·5) (6/7)	390·3 (0·2) (3/7)	394·2 (0·3) (4/7)
401·5 (0·3) (5/7)	410·9 (0·6) (13/13)	417·2 (0·2) (13/18)	422·3 (0·2) (5/10)
430·8 (0·3) (5/10)	437·4 (0·6) (9/10)	444·7 (0·6) (8/10)	450·3 (0·7) (8/10)
453·6 (0·4) (6/10)	459·3 (0·4) (7/10)	463·5 (0·2) (3/10)	467·3 (0·4) (6/8)
477·2 (0·9) (8/8)	487·4 (0·2) (3/8)	496·3 (0·8) (8/8)	507·9 (0·6) (7/8)
515·4 (0·4) (6/8)	518·9 (0·4) (7/7)	527·6 (0·3) (6/7)	538·9 (0·8) (7/7)
553·3 (0·7) (7/7)	564·4 (0·5) (6/7)		

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* See in this connection Lindsay and Voorhees, 'Phil. Mag.,' vol. 6, p. 910 (1928) and Coster and Wolf, 'Nature,' vol. 124, p. 652 (1929).

§ 4. *Critical Potentials for Copper.*

The copper target used was of pure electrolytic copper. With this metal, Thomas and Compton (*loc. cit.*) did not proceed above 268·5 volts, except for some values above 800 volts. From 100 volts up to this range, it will be noted from Table III given below that the values obtained here agree with those of Compton and Thomas.

It will be seen from Table III that, as has been pointed out above, the agreement in the region below 250 volts is very good. The inflection at 197·1

Table III.

Authors	107·3 (1·0) (3/3)	111·0 (0·7) (3/3)	—	117·8 (0·6) (3/3)
Compton and Thomas	108·2 (1·8)	111·0 (1·4)	115·2 (1·8)	117·8 (1·5)
Authors	128·0 (1·5) (3/3)	133·5 (1·8) (3/3)	139·5 (0·8) (4/4)	148·3 (0·9) (3/3)
Compton and Thomas	127·1 (1·4)	132·9 (0·9)	140·6 (1·5)	148·4 (1·4)
Authors	157·4 (0·9) (7/7)	—	166·3 (1·1) (7/7)	178·4 (0·7) (7/7)
Compton and Thomas	157·1 (1·4)	164·6 (1·6)	168·3 (1·1)	178·6 (1·5)
Authors	188·0 (0·6) (7/7)	197·1 (1·3) (6/7)	205·3 (0·6) (7/7)	217·1 (0·5) (4/4)
Compton and Thomas	188·8 (1·7)	—	204·8 (1·4)	216·8 (1·4)
Authors	222·0 (0·6) (3/4)	228·6 (0·8) (3/4)	231·8 (0·4) (2/4)	237·3 (0·6) (3/4)
Compton and Thomas	221·6 (1·5)	228·7 (1·5)	—	235·6 (1·9)
Authors	243·2 (0·9) (4/4)	251·4 (0·8) (3/3)	—	258·0 (0·9) (3/3)
Compton and Thomas	244·6 (1·3)	250·3 (1·6)	254·8 (1·3)	—
Authors	268·8 (0·9) (4/4)	274·6 (0·9) (7/7)	278·3 (0·7) (7/7)	285·1* (1·0) (7/7)
Compton and Thomas	268·5 (1·3)	—	—	—
Authors	295·0 (0·8) (5/6)	304·6 (0·9) (6/6)	310·0† (0·9) (5/6)	315·4† (0·7) (5/6)
Authors	319·6 (0·8) (11/12)	327·1 (0·7) (6/6)	331·4 (0·2) (4/6)	341·6 (1·1) (6/6)
Authors	349·7 (0·7) (6/6)	359·8 (0·7) (6/6)	366·9‡ (0·4) (6/6)	375·8 (0·9) (6/6)
Authors	382·9 (0·9) (7/7)	391·3 (0·9) (7/7)	394·2 (0·8) (2/7)	399·1 (0·7) (7/7)
Authors	407·2 (0·8) (7/7)	417·3 (0·9) (7/7)	425·6 (0·8) (6/6)	430·4 (1·2) (5/6)
Authors	435·8 (0·6) (4/6)	443·8 (1·0) (6/6)	458·2 (1·2) (6/6)	463·4 (0·3) (2/6)
Authors	473·9 (0·9) (5/6)	482·7 (0·9) (6/6)	491·0 (0·9) (5/6)	496·8 (0·3) 2/6)
Authors	505·4 (0·9) (6/6)	517·5 (1·0) (6/6)	538·0 (1·3) (6/6)	550·1 (1·1) (6/6)
Authors	582·4 (1·5) (7/7)	⟵ (0/7) ⟶	832·9 (1·3) (4/4)	921·5 (2·0) (5/5)
Compton and Thomas	—	—	820·4 (1·4)	929·0 (2·2)
Authors	1014·0 (1·6) (3/3)	—	—	—
Compton and Thomas	1017·0 (2·0)	—	—	—

* This appears as 282·1 (0·6) (4/7) + 286·5 (0·7) (4/7) on four of the seven curves.
† These appear as a single inflection on the other curve.
‡ Probably double.

was found to be a strong one, but this has not been recorded by Thomas. Two weak inflections, one at 231·8 volts and the other at 258·0, are also observed. On the other hand, the inflections at 115·2 and 254·8 volts recorded by Compton and Thomas have not been found. The value at 166·3 may be taken to be the unresolved blend of 164·6 and 168·3 recorded by them. Between 268·8 and 582·4 a large number of inflections have been obtained. But there is a sudden jump in the range from 582·4 to 832·9 volts. No inflections have been detected in this range, although much of it was gone over carefully seven times and the remainder at least three times.

Above 800 volts, inflections have been obtained at 832·9, 921·5 and 1014·0 volts. These agree closely with the values of Thomas, namely 820·4, 929 and 1017 volts. An examination of the X-ray level values of Thoraeus (*loc. cit.*) may help us to find out the origin of these inflections. His emission data give, for the transition from $L_{II\ III}$ to $M_{IV\ V}$ levels, the value of 938·6 volts. This is nearly equal to 929 volts recorded by Thomas and 921·5 volts observed here. A transition from $L_{II\ III}$ to the M_I level would require an energy of 823·7 volts, which agrees with 820·4 volts of Thomas and our value of 832·9 volts. The break at 1013·9 volts should be due to a transition from L_I to $M_{II\ III}$ levels, the calculated value being 1021 volts.

It is thus seen that all the inflections above 800 volts closely approximate to the hard X-ray values calculated from the data of Thoraeus. This region is also marked by the absence of a large number of values in contrast to the regions at lower potentials.

§ 5. *Critical Potentials of Tungsten.*

The question arose whether the elements having much higher atomic numbers would behave in the same manner as the iron group and copper, and tungsten was chosen for investigation.

The range from 20 to 540 volts was examined. The effect on the photoelectric plate below 20 volts was so weak that no reliable readings could be taken. The observed inflections are given in Table IV.

The results for tungsten are given corrected in volts. There were no inflections between 524 and 600 volts. In the range 0 to 600 volts the number of inflections for W is seen to be comparable with that for copper and the iron group. It is obvious from the large number and distribution of these that they have nothing much to do with the Bohr levels.

Table IV.—Critical Potentials of Tungsten.

Volts (intensity).			
24·7 (0·8) (7/7)	29·3 (0·4) (5/7)	35·6 (0·9) (7/7)	39·4 (1·1) (7/7)
43·8 (0·6) (7/7)	52·5 (0·4) (7/7)	60·1 (0·5) (5/7)	70·2 (0·3) (7/7)
76·3 (0·7) (11/12)	85·7 (0·4) (5/7)	90·1 (0·5) (5/7)	95·0 (0·4) (5/7)
102·6 (0·7) (6/7)	106·9 (0·3) (2/7)	113·8 (0·7) (5/5)	117·7 (0·4) (3/5)
122·9 (1·0) (9/11)	127·6 (0·7) (9/11)	132·6 (0·7) (9/9)	139·8 (0·4) (5/6)
142·8 (0·8) (5/6)	148·0 (0·6) (6/6)	153·9 (0·6) (4/4)	161·3 (0·5) (4/4)
166·4 (0·4) (9/11)	170·7 (0·6) (11/11)	178·8 (0·6) (10/10)	188·1 (0·6) (7/7)
193·8 (0·4) (4/7)	200·1 (0·8) (7/7)	204·3 (0·9) (6/6)	211·8 (0·5) (5/6)
218·2 (0·1) (2/6)	222·5 (0·8) (7/7)	233·7 (0·7) (7/7)	241·0 (1·2) (7/7)
246·6 (0·4) (4/7)	255·2 (0·7) (7/7)	257·8 (0·2) (2/7)	267·2 (0·4) (6/7)
272·9 (0·5) (8/11)	277·9 (0·2) (2/8)	283·5 (0·7) (6/6)	291·2? (0·6) (6/6)
307·7 (0·4) (5/6)	314·3 (0·6) (4/5)	317·5 (0·7) (4/4)	322·1 (0·4) (4/8)
326·1 (0·3) (5/8)	337·5 (0·6) (8/8)	350·7 (0·4) (7/8)	357·5 (0·5) (6/8)
367·7 (0·4) (4/4)	373·6 (0·8) (6/6)	379·2 (0·4) (3/6)	382·4 (0·2) (2/6)
385·7 (0·5) (5/6)	398·0 (0·5) (6/6)	405·5 (0·7) (6/6)	411·7 (0·7) (4/6)
416·7 (1·1) (6/6)	426·0 (0·5) (5/5)	465·7 (0·5) (5/5)	495·9 (0·4) (10/11)
523·2 (0·3) (7/8)			

§ 6. *Impure Copper.*

A possible way of reducing the number of discontinuities to be accounted for is to attribute some of them to the presence of impurities. In order to test this possibility experiments were made with impure copper.

The specimen out of which the target was cut was analysed spectroscopically by Dr. G. B. Bandopadhyaya, and from the lines obtained it was concluded that it contained nearly 1 per cent. of iron and $\frac{1}{2}$ per cent. of nickel, besides several other minor impurities. The range of applied potential over which tests were made was from 150 to 270 volts and from 490 to 560 volts. The results are collected in Table V. The critical potentials already found for pure copper and the values of Compton and Thomas are also given for comparison.

It is evident from the coincidence of most of the values that an impurity of 1 per cent. of iron and $\frac{1}{2}$ per cent. of nickel is not sufficient to bring in the characteristic inflections of these metals. The value of 219·4 volts may be the unresolved blend of 217·1 and 222·0 volts corresponding to pure copper. The values of 196·3 and 257·5 have been obtained both for pure and impure copper. But, as has been mentioned, these have not been recorded by Compton and Thomas. There are only three values which have been obtained in addition to those corresponding to the pure metal. These are at 182·6, 192·3 and 265·1 volts. Thomas obtains for iron values at 181·6 and 192·3 volts, and for nickel a value at 265·9 volts. It seems likely that the three inflections are due to the impurities of iron and nickel.

Table V.—Critical Potentials for Impure Copper.

Authors, for impure Cu.		Authors, for pure Cu.		Compton and Thomas, for pure Cu.	
Volts.	Intensity.	Volts.	Intensity.	Volts.	Intensity.
156·7	(1·0) (5/5)	157·4	(0·9) (3/3)	157·1	(1·4)
				164·6	(1·6)
		166·3	(1·1) (7/7)		
169·5*	(0·9) (5/5)			168·3	(1·1)
176·1	(0·7) (3/5)	178·4	(0·7) (7/7)	178·6	(1·5)
182·6	(1·0) (5/5)				
187·9*	(1·2) (5/5)	188·0	(0·6) (7/7)	188·8	(1·7)
192·3	(1·2) (5/5)				
196·3	(1·2) (5/5)	197·1	(1·3) (6/7)		
204·3	(1·3) (5/5)	205·3	(0·6) (7/7)	204·8	(1·4)
		217·1	(0·5) (4/4)	216·8	(1·4)
219·4	(1·0) (6/6)				
		222·0	(0·6) (3/4)	221·6	(1·5)
227·5	(1·0) (6/6)	228·6	(0·8) (3/4)	228·7	(1·5)
		231·8	(0·4) (2/4)		
236·8*	(1·1) (6/6)	237·3	(0·6) (3/4)	235·6	(1·9)
243·5	(0·7) (3/6)	243·2	(0·9) (4/4)	244·6	(1·3)
251·2*	(1·5) (6/6)	251·4	(0·8) (3/3)	250·3	(1·6)
257·5	(1·0) (5/6)	258·0	(0·9) (3/3)	254·8	(1·3)
265·1	(0·7) (2/6)				
268·5	(0·9) (3/3)	268·8	(0·9) (4/4)	268·5	(1·3)
498·3	(0·7) (3/5)	496·8	(0·3) (2/6)		
506·7	(1·4) (5/5)	505·4	(0·9) (6/6)		
516·3	(0·6) (3/5)	517·5	(1·0) (6/6)		
537·8	(1·3) (5/5)	538·0	(1·3) (6/6)		
552·3	(0·8) (3/3)	550·1	(1·1) (6/6)		

* Each of these appears to be double on one curve.

The excitation of soft X-rays is essentially a surface property, only a few layers at the surface taking part in the phenomenon. What, therefore, really counts is the surface impurity and not the volume impurity. Richardson and Chalklin have shown in their second paper (*loc. cit.*) that the characteristic values may be completely altered by depositing one element over another. In the target of impure copper it is possible, although not probable, that there might have been large impurities on the surface. However, it is very difficult to say why these three values alone have appeared, since it is found from the tables of inflections for iron and nickel that these inflections do not have any marked intensity.

One point in the experimental technique may be mentioned here. The usual method adopted to de-gas the metal parts other than the target and filament is to heat the tube strongly with a blowpipe flame with a good vacuum inside. It is possible that this might cause the nickel from the shield to condense on the target. In these experiments this procedure was not adopted. The tube was heated strongly with a Bunsen burner. At this temperature the vapour pressure of nickel is very low and there is little likelihood of the condensation of nickel on the target.

The results of these experiments make it unlikely that any considerable proportion of the large number of inflections observed can be attributed to the presence of small amounts of impurities.

§ 7. *Variation of* i_p/i_t *with* i_t.

In the course of this investigation the variation of the ratio i_p/i_t with i_t was carefully examined. The thermionic current i_t was maintained under constant voltages but varied by altering the heating current. The results for nickel and tungsten targets for various voltages between 70 and 585 are shown in figs. 4 and 5. Curves of the same type were also got with copper.

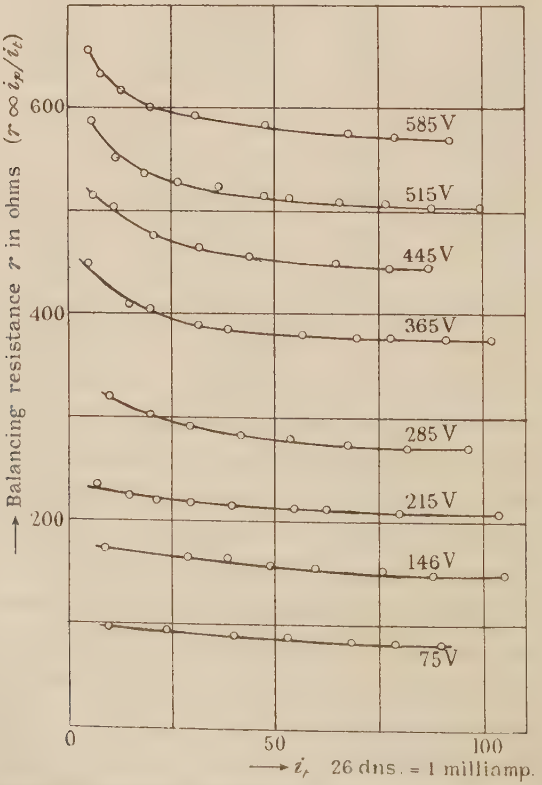

FIG. 4.—Curves between i_p/i_t and i_t for nickel. The applied potentials are the mean corrected values.

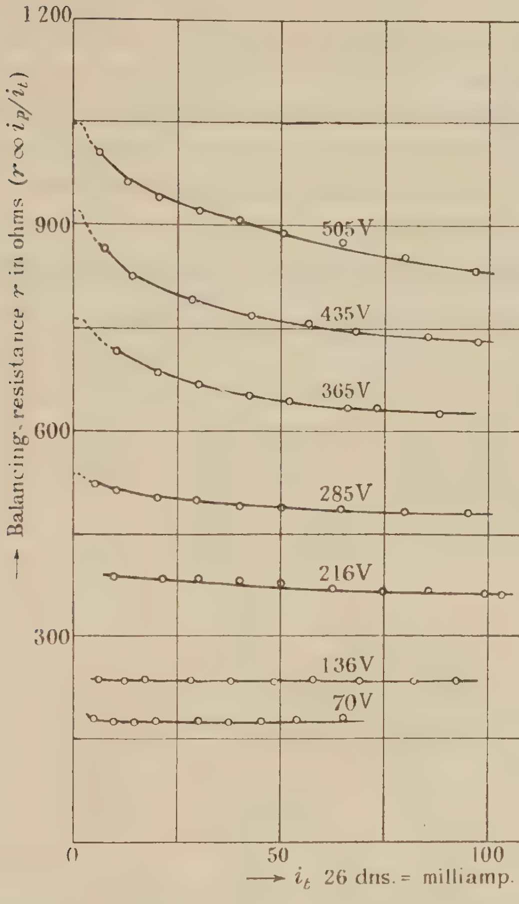

FIG. 5.—Curves between i_p/i_t and i_t for tungsten. The applied potentials are the mean corrected values.

The ratio was actually measured by finding the resistance r required to balance the potential drop Ri_p due to the photoelectric current i_p. i_p/i_t is then given by r/R.

There is a slight tendency for i_p/i_t to increase as i_t diminishes. This is most marked at high voltages and low thermionic currents. The lowest currents we could use conveniently in this apparatus were about 0·2 milliamp. Nakaya* using small currents between 15 and 60 microamps. found the ratio i_p/i_t to be almost constant. As a reconciliation of these results we suggest the dotted continuation of the curves shown in fig. 5.

We believe that the apparent variation of i_p/i_t with i_t is due to changes in the distribution of the electronic discharge over the surface of the target with different currents and that if these effects could be eliminated, i_p/i_t would be constant for a given voltage. In any event the changes observed are small, at most about 25 per cent. at the highest voltages over the whole range from 0 to 4 milliamps. It should also be noticed that the changes of i_p/i_t are quite regular and not of the kind which would be expected to give rise to discontinuous changes in the i_p/i_t : V diagrams.

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* 'Roy. Soc. Proc.,' A, vol. 124, p. 616 (1929).

§ 8. *Variation of i_p/i_t with the Inclination of the Target.*

The target was placed in different positions starting with the position shown as $\theta = 0$ in fig. 1. The variation of i_p/i_t with the position of the target from 0 to 180 degrees in the case of nickel is shown in fig. 6. The angles made by the target with the initial position were measured by means of a graduated paper strip outside the tube and a point on the soft iron piece used for rotating the target. They may be in error by about 4°.

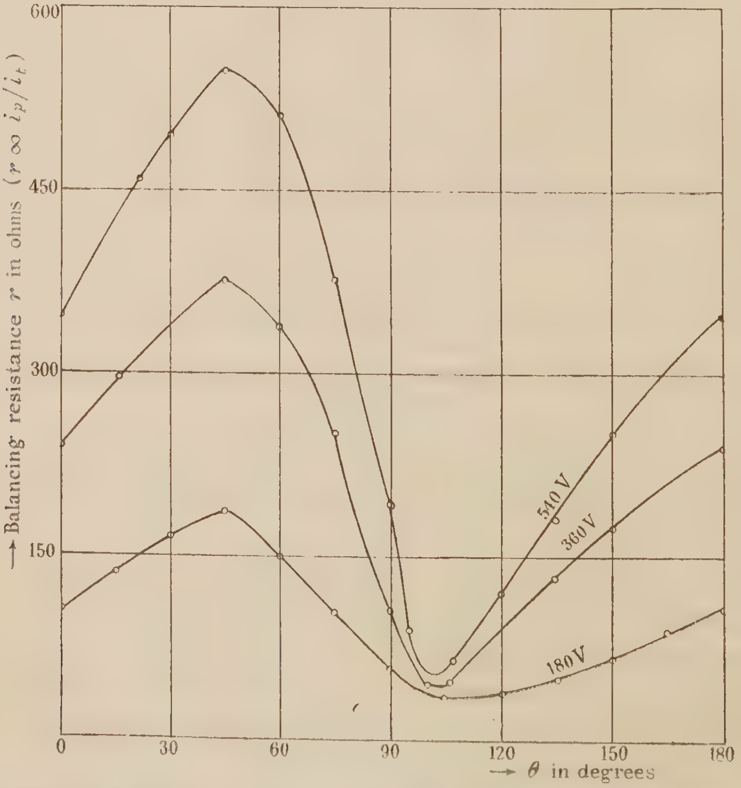

FIG. 6.—Curves showing the variation of i_p/i_t with the position of the target at applied potentials of 180, 360 and 540 volts.

It is improbable that the curves of fig. 6 will admit of any very detailed quantitative interpretation. The problem is complicated by the change in the distribution of the electron current about the surface of the target as this is rotated. The experiments were made with constant voltages of 180, 360 and 540 respectively between the filament and the target. However, the thermionic current, with a constant voltage, varied very little as the target was rotated. The relative position of the various electrodes in the tube during this experiment is shown, both in plan and elevation, to scale in fig. 7.

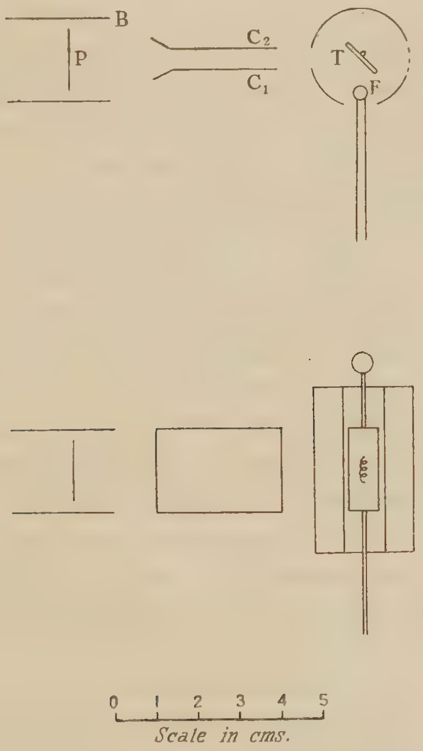

Fig. 7.

One thing at any rate is clear. The value of i_p/i_t is a maximum when the angle θ is equal to 45°. It is probable that for angles between 45° and normal incidence, possibly for a wider range of angles, the value of i_p/i_t is a maximum when the normal to the target bisects the angle between the line joining the middle of the filament to the middle of the target and the line passing through the axis of the slits.

Except where it is definitely stated to be otherwise, in all the experiments described in this paper the target was always kept in the position $\theta = 45°$

at which the ratio is a maximum. In this position any slight displacement of the target or other parts of the system will have least influence on the results. The position of the target was fixed by a pin and a set of grooves, as described by Richardson and Robertson.*

§ 9. *The Intensity of the Inflections.*

Although the critical potentials measured by us show on the whole a good agreement with the values given by Thomas there is little or no correspondence between our estimates of the intensities of the inflections and his. This divergence may arise from some difference in the heat treatment of the targets, since the following experiments with the cobalt target show that the intensities depend very much on the previous treatment of the target.

The cobalt target was finely polished and then sealed into the tube. Care was taken in de-gassing the target to keep it at a dull red heat. It was de-gassed at this temperature for several days and then the experiments were made. It was found that in the range from 200 to 460 volts the inflections obtained were very weak. In fact most of them can only be found by employing the method of Thomas, namely, drawing the curves with reference to a line inclined to the voltage axis as near as possible to the curve. In the range above 400 volts no inflections could be detected even when the sensitivity was increased by drawing the curves in this way. On the other hand, when the target in the process of de-gassing was raised to bright red heat, the intensities of the inflections below 400 volts became much larger and were obtained by plotting the readings of the electrometer scale directly against the applied voltage. Furthermore, points at potentials above 400 volts were obtained after keeping the target at bright red heat for some hours.

Typical curves are given in figs. 8 and 9. Curve (*a*) in fig. 8 was obtained with the target when the de-gassing was done without raising it to a bright red heat. It will be seen that the intensities of the inflections are small and some inflections can hardly be observed. Curve (*b*) shows the same curve drawn in accordance with the method of Thomas. Curve (*c*) gives the relation between i_p/i_t and the applied potential when the target was previously de-gassed at a bright red heat. It will be seen that the inflections are obtained more clearly than in curve (*a*) because of much greater intensity. In fig. 9 corresponding curves are given for the region 400 to 450 volts. These show that after de-gassing by heating the target to a comparatively low temperature the inflections do not appear ; but they are present prominently if the same target is heated to redness before the observations.

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* 'Roy. Soc. Proc.,' A, vol. 115, p. 281 (1927).

It is probable that the intensification of the inflections is caused by the recrystallisation of the target surface rather than by the removal of gas which might have not been sufficiently eliminated by the process of de-gassing at a low temperature. In the first place this process was carried on for several days before the tests were made. Secondly, after the tests, the targets were suddenly raised to a bright red heat by electron bombardment and there was no indication on the McLeod gauge of even a small increase of pressure.

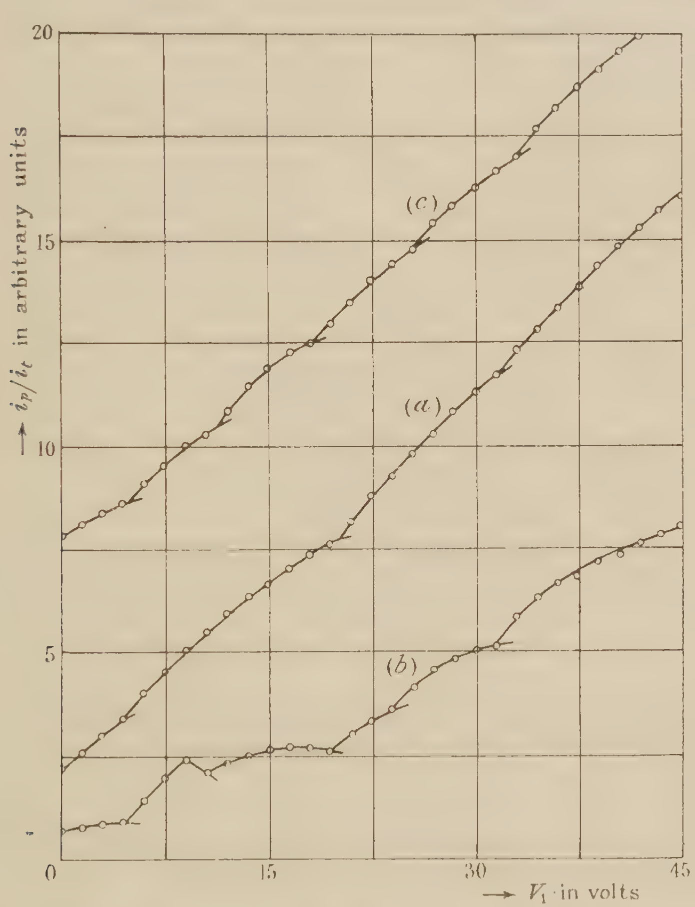

FIG. 8.—i_p/i_t curves for cobalt. $V_2 = 256$ volts. (*a*) For metal de-gassed at low temperature. (*b*) Same drawn according to the method of Thomas. (*c*) For metal de-gassed at high temperature.

This dependence of the intensity of the inflections on the previous heat

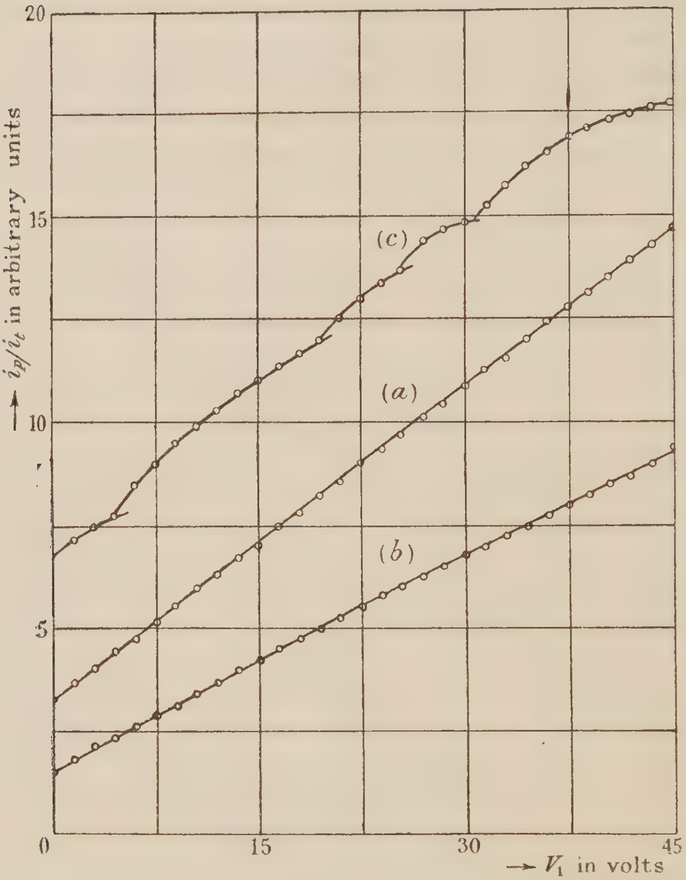

FIG. 9.—i_p/i_t curves for cobalt. $V_2 = 406 \cdot 6$ volts. (*a*) For metal de-gassed at low temperature. (*b*) Same drawn according to the method of Thomas. (*c*) For metal de-gassed at high temperature.

treatment may account for much of the divergence between results of different observers who have measured these critical potentials.

§ 10. i_p/i_t *Curves for Tungsten and Copper over the whole range.*

It was next thought that it would be interesting to draw a curve between i_p/i_t and the applied potential over the whole range from 30 to 1050 volts in the case of copper and 30 to 600 volts for tungsten. Experiments for the determination of i_p/i_t were made at intervals of about 20 to 50 volts. The value of the balancing resistance r was taken as a measure of i_p/i_t. The determinations were made under the same conditions, as far as possible, and the thermionic current was kept nearly the same in all the measurements at about 2·5 milliamperes.

Curves between i_p/i_t and applied potential (uncorrected) are shown for copper and tungsten in fig. 10. It is found that in the case of copper inflections occur at about 100, 675, 825 and 920 volts. The continuation of the curve above 1000 volts is not clear and we shall therefore consider these four values, leaving aside the discontinuity at 1013·9 volts recorded already. The values 825 and 920 volts almost coincide with 832·9 and 921·5 tabulated above (see Table III). The value near 100 volts may be attributed to transitions from the M_1 level to the boundary of the atom. There is a value at 675 volts which is fairly

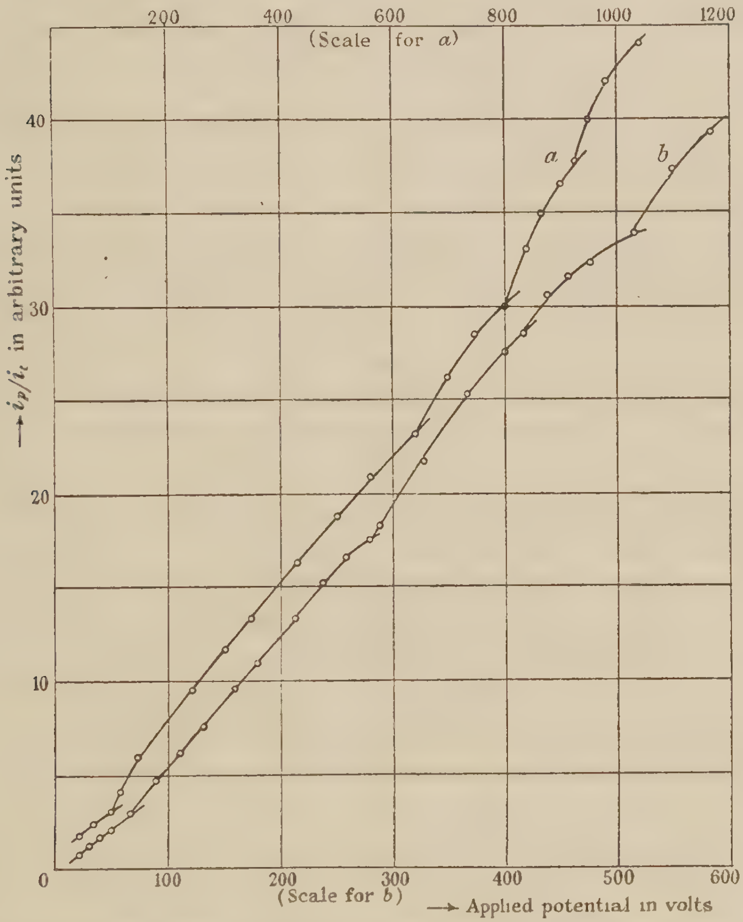

Fig. 10.—(*a*) Curve for copper in the range 0–1050 volts. (*b*) Curve for tungsten in the range 0–600 volts.

definite in the neighbourhood and which did not appear before. The method being rough and the steps being large, the error in these values may be considerable. The nearest theoretical X-ray level value is 713 volts due to a transition of an electron from the L_{III} to M_I orbit. It is surprising that all other values are smoothed out while these four inflections are left.

The same behaviour was observed in the case of tungsten. Inflections are found at about 75, 275, 420 and 525 volts. These, it will be noticed on referring to the data of Nishina given above, fall near $O_{II\ III}$ (70·5 volts) and O_I (77·3 volts), N_{IV} (254·9 volts), N_{III} (447·5 volts), $N_{II} - O_I$ (438·0 volts), $N_I - O_{II\ III}$ (520·7 volts) and N_{II} (515·3 volts).

It looks very probable that where curves are drawn at such large intervals, the inflections tend to occur at the values coinciding with the electronic transition values mentioned above. This explains the results of Richardson and Chalklin, who obtained these values in their experiments with tungsten. Besides these they obtained seven other inflections, some of which are thought not to be due to tungsten. The experimental method adopted by them was fairly sensitive. It will be noticed from their published curves (their first paper, *loc. cit.*) that they got inflections coincident with X-ray term values when they took large intervals. Of the seven additional inflections, two are very variable and the other five have very low intensities. With one exception, these weak inflections were only obtained on taking 2-volt intervals.

It appears from these experiments that when most of the inflections are smoothed out by choosing larger intervals the values coinciding with the X-ray term values still remain. If this result can be established generally, it shows that the general trend of the curves is governed by the X-ray level structure of the element, although the detailed inflections are due to something else.

The Excitation of Soft X-Rays from a Single Crystal Face of Nickel.

By O. W. Richardson, F.R.S., Yarrow Research Professor of the Royal Society, and S. Ramachandra Rao, M.A., King's College, London.

(Received March 1, 1930.)

During the progress of our experiments* on polycrystalline metals the newly available evidence suggested that crystalline structure might have much to do with the soft X-ray inflections. The fact that the intensity of the inflections was increased by heating the targets to a high temperature by electron bombardment, and that, as had been shown by the experiments of Dr. Nakaya,† this same treatment resulted in the formation of a large number of fresh crystal faces on the surface seemed particularly suggestive in this respect. We resolved, therefore, to make experiments on a single crystal surface in the hope that this would result in a simplification of the phenomena.

The single crystal used in these experiments‡ was kindly lent to us by Dr. H. H. Potter of the University of Bristol. Nickel crystals are of the face-centred cubic type. The face of the crystal which was used was prepared by Dr. Potter and represented the 100 plane.

The soft X-rays excited from the crystal face were investigated in the same way as those from the ordinary metals had been. Since the face of the crystal was only about 12 mm. by 6 mm., a new shield with a smaller aperture 10 mm. by 4 mm. was used. This change was to ensure that the soft X-radiation excited on the 100 face alone might be effective on the photo-electric detector. By geometrical calculations it was found that the proportion of the total radiation reaching the detector in this case was only four-tenths of the corresponding quantity in the previous measurements with ordinary metals.

Great care was taken not to heat the crystal during de-gassing to temperatures higher than about 1000° K. by keeping it at a dull red heat. Heating to higher temperatures would result in the breaking down of the crystal.

Experiments were at first conducted in the range from 0 to 300 volts with an average thermionic current of 1·5 milliamperes. The photo-electric current was too small for satisfactory measurements below about 45 volts. Several graphs were drawn between i_p/i_t and the applied potential, and it was found that in the range 45 to 300 volts only five inflections occurred. These values, along with their average intensities (in brackets) are shown in rows 2 and 5 in the following table. The inflection at 94·3 volts was weak, while the other four were relatively strong.

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* 'Roy. Soc. Proc.,' A, *supra*, p. 16.

† 'Roy. Soc. Proc.,' A, vol. 124, p. 616 (1929).

‡ A preliminary account of some of the results was published in 'Nature' (vol. 123, p. 344 (1929).

Table I.

Polycrystalline Ni (Thomas)	57·4 (3·1)	65·6 (2·0)	71·9 (1·5)	79·8 (1·7)	87·2 (1·6)
100 face (at 1·5 milliamp.)		63·8 (1·2)	72·2 (0·9)		
100 face (at 3 milliamp.)		63·2 (1·9)	72·0 (1·3)		
Polycrystalline Ni (Thomas)	91·2 (0·9)	94·9 (1·2)	98·3 (1·7)	106·5 (2·0)	116·6 (1·2)
100 face (at 1·5 milliamp.)		94·4 (0·1)		106·2 (1·2)	116·0 (1·0)
100 face (at 3 milliamp.)		94·3 (0·5)		106·5 (1·4)	116·1 (1·1)
Polycrystalline Ni (Thomas)	127·0 (1·0)	133·7 (1·4)	139·6 (1·4)	145·0 (1·3)	156·8 (1·4)
100 face (at 1·5 milliamp.)	—	—	—	—	—
100 face (at 3 milliamp.)	129·0 (0·4)			144·8 (0·4)	155·9 (0·4)
Polycrystalline Ni (Thomas)	167·3 (1·0)	178·2 (1·2)	186·2 (1·2)	197·7 (1·8)	217·7 (1·3)
100 face (at 1·5 milliamp.)	—	—	—	—	—
100 face (at 3 milliamp.)		179·9 (0·3)	186·0 (0·3)		217·7 (0·3)
Polycrystalline Ni (Thomas)	228·2 (1·1)				

Subsequently the experiments were repeated over the entire range at a higher thermionic current with an average value of 3 milliamperes. This would, no doubt, mean a greater sensitivity, and as a result several more inflections were obtained. These are shown in Table I above, rows 3, 6 and 9. The corresponding intensities are given in brackets. The four inflections at 63·8, 72·2, 106·2 and 116·0 have again appeared, while that at 94·4 has become stronger. In rows 1, 4 and 7 are given the values in the range from 55 to 230 volts obtained by Thomas for ordinary nickel.

It will be seen that all the inflections found with the crystal are quite close to one or another of Thomas's values. At the same time many of Thomas's strong inflections are entirely absent on the curves given by the crystal. We deduce from this that the inflections are properties of the crystal faces, and that those given by the polycrystalline material represent a mixture of effects characteristic of the different faces present.

Since the experiments described in the present paper were finished we have concluded that there is one direction in which the experimental evidence requires strengthening. The experiments on polycrystalline cobalt showed that the intensities of the inflections were very dependent on the previous treatment of the target. It may, therefore, be urged that the difference between the effects got with the nickel crystal and those got by Thomas arises from some difference in the treatment of the specimens in the two cases. It is intended therefore to make further experiments with the nickel crystal and with a polycrystalline nickel target in which both specimens are subjected to identical treatment. We are unable to do this at once, as it necessitates some alteration in the present structure of the apparatus which is now being used for another purpose. It is also intended to make experiments on other crystal faces.

In fig. 1 are given some typical curves between i_p/i_t and the applied potential in the ranges 50 to 85 and 90 to 125 volts.

Measurements have also been made on the intensity of the soft X-radiation at different voltages by taking readings at rather widely separated intervals

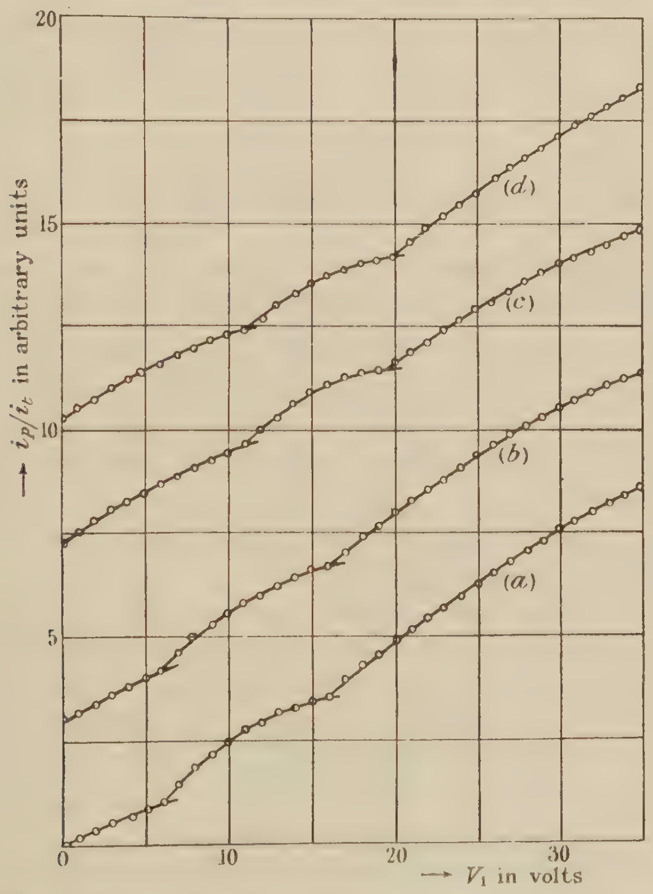

FIG. 1.—Curves between i_p/i_t and applied potential for the nickel crystal, face 100. (*a*) and (*b*) V_2 = 50 volts. (*c*) and (*d*) V_2 = 90 volts. The ordinates are entirely arbitrary.

in the range 50–400 volts. In fig. 2, curve (*a*) shows the variation of i_p/i_t with applied potential in this range for the 100 face of the crystal. It will be seen that the curve shows only one inflection prominently, at 115 volts. The " fine structure " of the type shown in fig. 1 is, of course, not discoverable when such wide steps are taken. Experiments were made later to find the intensity-potential curve for ordinary nickel (polycrystalline) with the same shield as for the crystal. The result is shown in curve (*b*) in fig. 2. The thermionic currents at different potentials were made nearly equal to those in the case of the crystal to get identical conditions.

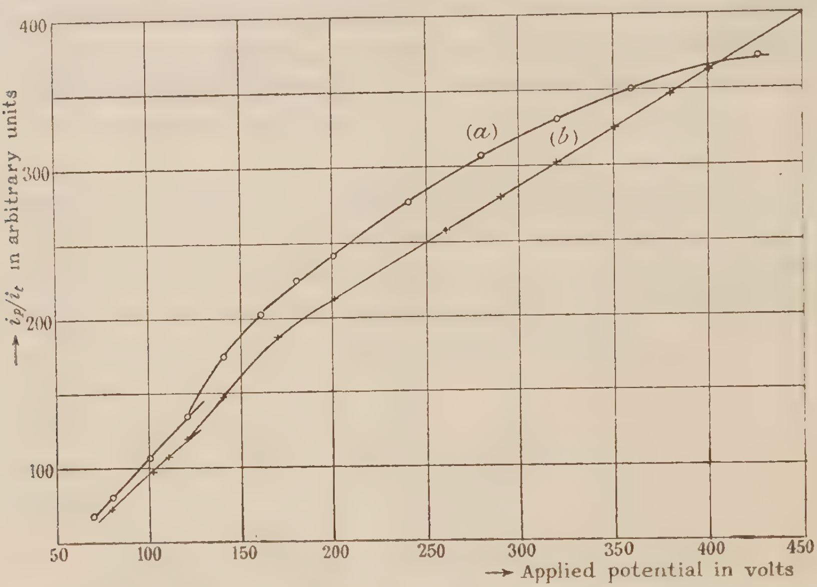

FIG. 2.—Soft X-ray intensity curves for a polycrystalline nickel target (*b*) and for a nickel crystal face 100 (*a*). The ordinates are the same for both cases.

It will be seen that throughout the range below 400 volts, the intensity of the soft X-radiation from the crystal is greater than for the ordinary metal. The shape of the curve, however, differs considerably. The curve (*b*) shows that the intensity varies roughly as the applied potential, thus tending to obey the equation of Kramers as modified by Richardson and Chalklin* and Richardson and Robertson.† But on the other hand the curve (*a*) behaves differently. It shows a saturating tendency at higher potentials.

It will be recalled that Richardson and Robertson‡ and Nakaya (*loc. cit.*)

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* 'Roy. Soc. Proc.,' A, vol. 110, p. 273 (1926).

† 'Roy. Soc. Proc.,' A, vol. 115, p. 280 (1927).

‡ 'Roy. Soc. Proc.,' A, vol. 124, p. 188 (1929).

showed that at high applied potentials the soft X-radiation for even ordinary metals evinced this tendency to attain saturation. The reason for this apparent violation of Kramers equation is unknown. It looks, however, as if the causes which operate may result in giving the saturating tendency at low potentials in the case of crystal faces and at relatively higher potentials in the case of polycrystalline faces.

Total Secondary Electron Emission from Polycrystalline Nickel.

By S. Ramachandra Rao, M.A., King's College, London.

(Communicated by O. W. Richardson, F.R.S.—Received March 1, 1930.)

1. *Introduction.*

The importance of secondary electron emission in its relation to the excitation of soft X-rays has been pointed out in a recent paper by Prof. O. W. Richardson.* He has shown that at every potential where there is an increased excitation of soft X-rays, there is correspondingly an increase in the emission of secondary electrons, and has discussed at some length the mechanism of the generation of secondary electrons. It was therefore felt that a much clearer idea of the phenomenon of soft X-ray excitation from metallic surfaces could be had by studying the secondary electron emission from polycrystalline and single crystal faces.

As early as in 1908 Richardson† showed that slowly moving electrons are reflected in considerable proportion from metallic plates. Davisson and Kunsman,‡ in a series of papers commencing from 1921, showed that at low voltages up to about 9 volts most of the secondary electrons were purely reflected electrons with velocities the same as the incident electrons. The percentage of the reflected electrons fell rapidly as the applied potential was increased above 9 volts, while that of low velocity electrons increased steadily. Farnsworth,§ with improved apparatus, added much valuable information regarding the generation of secondary electrons and the conditions operating in such cases. These observers showed that the total emission of secondary electrons from a metal surface depended on the applied potential, the nature of the surface and the previous heat treatment of the metal. They also found that the ratio of the secondary beam to the primary increases with applied potential and becomes greater than 1 after a certain potential, depending on the nature of the bombarded metal, is reached.

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* 'Roy. Soc. Proc.,' A, vol. 119, p. 531 (1928).

† 'Phil. Mag.,' vol. 16, p. 898 (1908) and 'Phys. Rev.,' vol. 29, p. 557 (1909).

‡ 'Phys. Rev.,' vol. 20, p. 111 (1922), and vol. 22, p. 242 (1923). See also 'Science,' vol. 64, p. 522 (1921).

§ 'Phys. Rev.,' vol. 20, p. 358 (1922); vol. 25, p. 41 (1925); vol. 27, p. 413 (1926) and vol. 31, pp. 405, 414, 419 (1928).

Even at a primary potential of about 30 volts the reflected electrons form about a tenth of the total secondary emission.

Petry* was the first to show that there might be a correspondence between the soft X-ray discontinuities and the secondary electron discontinuities. But later Farnsworth (*loc. cit.*) showed from his experiments that there was no such evidence for the existence of critical potentials in his work. However, the experiments of Krefft† made with great care showed that there were definite inflections and that these coincided with the soft X-ray discontinuities. A great improvement in his work was that the target could be kept hot during the experiments, and under these conditions there is no question of adsorbed gas on the surface at the time of taking readings.

In the following work the method of Krefft has been adopted with important improvements in one or two directions. Krefft used only one galvanometer for taking both the readings of the primary and secondary current. This is a disadvantage. The author has found that using two galvanometers, as was also adopted by Petry, is distinctly advantageous, since the stability of one spot can always be tested by looking at the other.

2. *Apparatus.*

The details of the apparatus are shown in fig. 1. The tube is of quartz made by the Thermal Syndicate. All the metal parts except the filaments were made of nickel. The filament F_1 consists of three turns of 2-ampere tungsten wire and gives the primary beam. A is a shield outside F_1 with an aperture of 7 mm. diameter. The part B constitutes the "electron gun" and consists of a cylindrical antechamber with an aperture 3·5 mm. diameter, and a uniform nickel tube with an internal diameter of 3·5 mm. It was thought that by having a short canal a strong and uniform beam of electrons could be got with only a very small percentage of low velocity electrons caused by the incidence of the primary electrons on the sides of the canal. The

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* 'Phys. Rev.,' vol. 26, p. 346 (1925) and vol. 28, p. 362 (1926).

† 'Phys. Rev.,' vol. 31, p. 199 (1928).

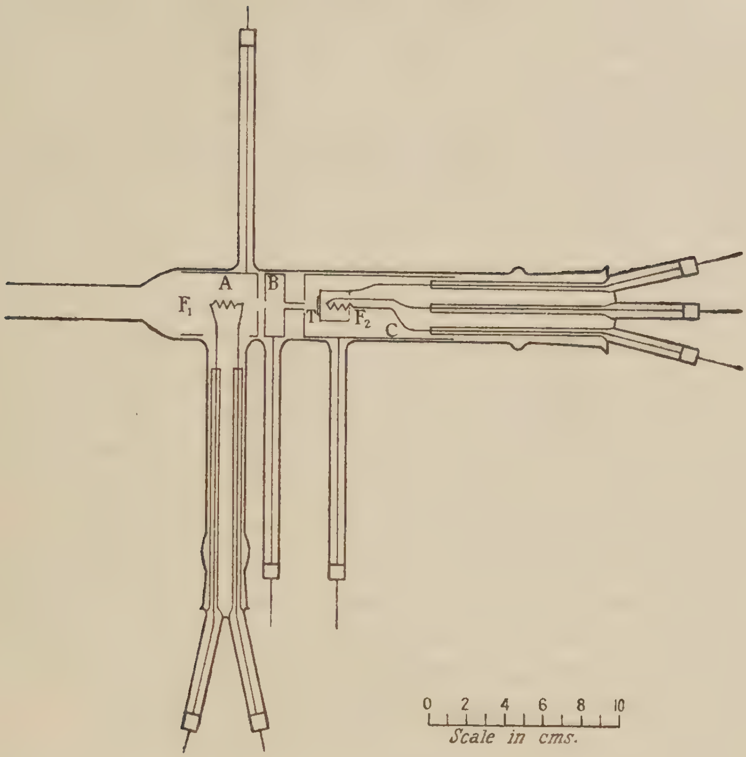

Fig. 1.—Secondary Electron Emission Apparatus.

consistency of the results obtained, as will be shown later, indicates that this assumption was justified.

The target T was fixed by screws to the closed end of a hollow nickel cylinder 15 mm. diameter and 15 mm. long. The distance from the face of the target to the end of the electron gun was 7 mm. and to the nearer end of the filament F_1, 4·5 cm. A 5-ampere tungsten filament F_2 within the nickel cylinder served to de-gas the cylinder and the target and also to keep the latter hot during the experiments whenever desired. C is a shield outside the cylinder to collect the secondary electrons.

3. *To find the Temperature of the Target.*

The first part of the experiment was to get an idea of the temperature of the target for any given heating current of the filament, F_2. This was done by conducting some initial experiments without the filament F_1 and the metal parts A, B and C. The junction of a thermocouple consisting of pure platinum wire and a wire of platinum with 10 per cent. of rhodium was inserted between the cylinder and the target. The ends of the couple were taken through the side tubes. When the target is heated a thermoelectric e.m.f. is generated between the ends of the couple and this was directly measured on a millivoltmeter. This standard thermocouple has been calibrated by the National Physical Laboratory* and hence, from the e.m.f. read, the temperature is estimated directly.

A calibration curve was drawn between the heating current through F_2 and the temperature of the target. In these experiments no potential was maintained between the cylinder and the filament. If, however, a potential is maintained there will also be the heating effect of the bombarding current. In the process of de-gassing, it would be advantageous to know the temperature of the target. This becomes particularly so in the case of the crystal target which should not be heated to temperatures higher than 1000° K. if it is to keep its structure. Keeping the applied potential at 540 volts a curve was drawn between the bombarding current and the temperature. Since at a constant potential the bombarding current depends on the current through F_2 no account need be taken of this in this curve. These calibration curves were drawn with the tube in perfect working order, the metal parts being well de-gassed and the pressure being less than 10^{-6} mm.

4. *Electrical Connections and Method.*

It was felt that a real test should be made with a polycrystalline target of nickel to see whether the existence of inflections in the secondary electron curves is real, and, if so, how far the values obtained coincide with those of Petry and the soft X-ray inflections of Thomas.† A sample of pure nickel was taken in the form of a plate 1 cm. square and $\frac{1}{2}$ mm. thick and was fixed on to the cylinder with screws after having been thoroughly polished. It was the same piece that was used in the calibration curves described above. After the calibration curves were drawn, the thermo-junction was removed and the metal parts were fitted as shown in fig. 1. The general methods of de-gassing were the same as those described by Richardson and Rao.‡

The electrical connections are shown in Fig. 2 and in principle are similar to those of Krefft. The heating current for F_1 was supplied by an insulated storage battery. The metal parts were heated by electronic bombardment wherever possible or otherwise by a burner. The galvanometers G_1 and G_2 recorded the primary and secondary electron currents i_p and i_s respectively.

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* Kaye and Laby, "Tables Phys. Chem. Constants," 4th ed., p. 50.

† 'Phys. Rev.,' vol. 26, p. 739 (1925).

‡ 'Roy. Soc. Proc.,' A, *supra*, p. 16.

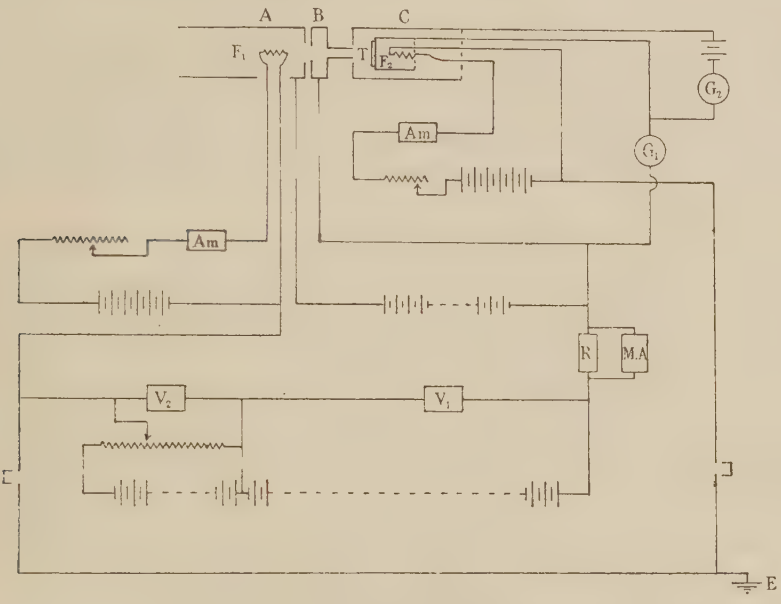

FIG. 2.—Secondary Electron Emission Connections.

These galvanometers had a sensitivity of about $6{\cdot}5 \times 10^{-9}$ amp. per millimetre on the scale. The currents were of the order of micro-amperes. To enable the readings to be taken at full sensitivity the galvanometers had balancing currents in the manner used by Petry. By making the resistance R_2 very large (a tenth of a megohm) when compared with that of the galvanometer (1000 ohms), the full sensitivity was retained. The potential between the filament F_1 and the target was applied in the same manner as in the soft X-ray work. If a test was to be made in the region 80 to 120 volts, V_1 was made 80 volts and the potential V_2 was gradually increased from 0 to 40 volts. The reverse currents in G_1 and G_2 were so adjusted that the spots of light were on the scales throughout the increase with as high a sensitivity as possible.

Preliminary experiments showed that by maintaining the shield C at 4 volts higher than the target all the scattered electrons could be collected.

The shield A around the filament F_1 was usually maintained at 50 volts higher than the canal and the target. In this manner a fairly strong electron beam was obtained even at moderate currents through F_1.

The following intervals were adopted : $\frac{1}{2}$-volt steps below 35 volts, 1-volt steps between 35 and 120 volts, $1\frac{1}{2}$-volt steps between 120 and 325 volts, and 2, 3 or 4-volt steps above 325 volts.

It will be noticed that the current reflected directly back through the opening of the shield C is lost. The observed value of the total secondary emission would be slightly smaller than the actual value. But since the solid angle subtended by the opening at the centre of the target is only about 3 per cent. of the entire solid angle, this decrease would not be considerable. In any event, the position of the inflections in the total secondary electron curve will not be affected.

We should also consider the electrons reflected from the shield C to the target and cylinder. This will decrease the observed secondary current. But it is known from Farnsworth's experiments that the secondary electrons have mostly low velocities. Preliminary experiments showed that an additional positive potential of 4 volts on the shield was enough to prevent any appreciable reflection or emission from the shield. It was found that by increasing this additional positive potential to 6 volts, in a particular experiment where the primary potential was 200 volts the increase in the secondary current was about 0·25 per cent. This was true at all the primary potentials used in this work. It can therefore be assumed that the secondary current reflected back or emitted again by the shield was practically negligible.

The ratio of the readings of the galvanometers G_2 and G_1 gives directly the ratio of i_s the secondary current to i_p the primary current. Graphs have been drawn between the applied potential and i_s/i_p at different ranges of the applied potential and several inflections have been obtained in the range below 540 volts.

Some corrections have to be applied to the readings of the voltmeter. The correction for the initial emission velocity of the electrons is about 0·25 volts at the temperature of the filament while there is further the correction for the drop in potential along the filament. This is quite similar to the case of the soft X-ray work. Also we should consider the contact difference of potential between the hot cathode and the nickel target. The actual value of this correction is not known definitely. An experimental determination of this correction was attempted by finding the negative potential to which the target must be raised above the positive potential to which it is subjected to prevent any electrons from reaching it from the filament. This value was found to be about +1 volt while Petry obtained a value of 0·8 volt.

In the following work the aim was to find whether there was any coincidence between the soft X-ray inflections and the secondary electron emission discontinuities. The readings given in Table II are therefore uncorrected, except for the drop in potential along the filament.

5. *Results for Polycrystalline Nickel.*

(*a*) *Variation of i_s/i_p with i_p.*—The variation of i_s/i_p was carefully studied as i_p was increased from about 0·2 micro-amperes to 5 micro-amperes, at applied potentials 50, 100 and 200 volts. The results are given in fig. 3.

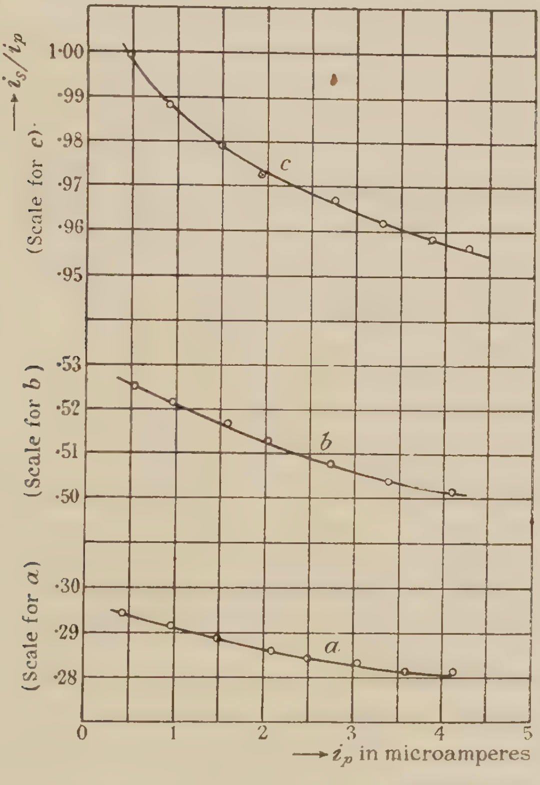

FIG. 3.—Curves between i_s/i_p and i_p for nickel: (*a*) at 50 volts; (*b*) at 100 volts; (*c*) at 200 volts.

It is found that at all the applied potentials, the value of i_s/i_p decreases a little as i_p is increased. This decrease is nearly 5 per cent. of the value at the lowest primary current in each of the three cases studied. This slight decrease may be explained as due to the fact that as the primary current is increased, more electrons pass through the nickel canal and hence the probability of the collision of the primary electrons with the sides of the canal is increased.

Hence some of the primary electrons will have a decreased velocity and hence i_s/i_p decreases.

In any case this small variation of i_s/i_p will not affect the measurements of the inflections made in these investigations.

(*b*) *Peaks below* 30 *volts.*—Over 100 curves were drawn from the data given by different experiments in various parts of the range from 0 to 540 volts and readings over the same range were taken on different days. In fig. 4 are drawn two typical curves in the region 1 to 30 volts. It is found that the secondary electron emission increases rapidly from 1 to 3 volts. The total emission then decreases rapidly up to 12 volts, giving, however, in a number of cases, another maximum at about 7 volts. From 12 to 15 volts the value remains practically constant, giving a feeble maximum at 14 volts. After 15 volts the total emission increases, giving rise to well-defined peaks at 18 and 26 volts. Above 30 volts no more peaks are obtained but there are a large number of inflections. Below is given a list of these peaks with an idea of their relative intensities.

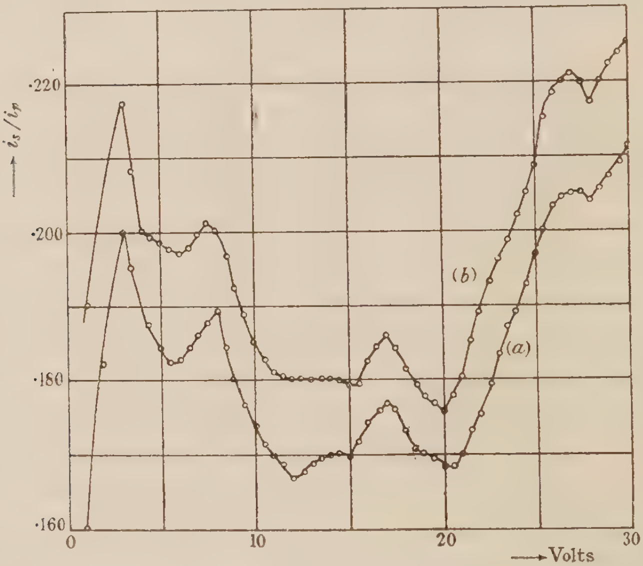

FIG. 4.—Curves between applied potential and i_s/i_p for ordinary nickel (polycrystalline) in the range 1 to 30 volts. The scale marked along the Y axis refers to curve (*a*). For the correct ordinates of curve (*b*), subtract 0·01 from the values marked.

Table I.—Secondary Electron Peaks for Nickel in the Range 1 to 30 volts.*

Potential in volts at which peaks occur.	Estimate of intensity.
3·0	Strong
7·0	Strong
14·0	Weak
18·0	Weak to Moderate
26·0	Moderate
30·0	Moderate

An interesting method of explaining these peaks has been given by Davis.† He considers that since the surface of the metal target is polycrystalline there will be all sorts of orientations of crystal faces. These faces may give rise not merely to reflection of electrons as Davis considered but also to diffraction in the manner shown by Davisson and Germer.‡ The various faces will contribute their reflection and diffraction effects similar to the Debye-Scherrer method of powder crystals and we thus have maxima corresponding to different orientations.

(*c*) *Inflections in the Range* 30 *to* 540 *volts.*—We shall now consider the applied potentials at which inflections appeared in the intensity-voltage curves. The uncorrected values are given in Table II in the first column. In the second column are given the intensities of the inflections estimated purely by the eye from the change of slope in the same manner as in the soft X-ray inflections. The values obtained by Petry for nickel by the secondary electron method and by Thomas for soft X-rays are also given for comparison.

It is seen that considering the difficulties of the method there is good agreement between the values of Petry and the author. Whereas Petry gets only 11 inflections in the range between 30 and 540 volts, as many as 25 have been obtained by the author in the same range.

A comparison with the soft X-ray inflections is, however, not so encouraging, the number of these being so large. However it may be seen that almost every value obtained in the secondary electron emission curve coincides with

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* [*Note added in proof.*—The values found are very close to the values of the maxima in the velocity distribution curves of the secondary electrons reflected with slightly reduced velocities recently reported by Rudberg for copper (' Roy. Soc. Proc.,' A, vol. 127, p. 134 (1930). Further experiments to test the connection between these phenomena are being instituted.]

† ' Nature,' vol. 123, p. 680 (1929); see also ' Proc. Nat. Acad. Sci.,' vol. 14, p. 460 (1928).

‡ ' Phys. Rev.,' vol. 30, p. 705 (1927).

Table II.—Secondary Electron Emission Discontinuities for Polycrystalline Nickel.

Author's values.		Petry's values (uncorrected).		Thomas's soft X-ray values (uncorrected).	
Volts.	Intensity.	Volts.	Intensity.	Volts.	Intensity.
30·8	1·2	30·0	2	29·6	2·2
				34·8	1·4
39·9	1·0			39·7	1·5
		43·2	3		
45·7	0·6			46·3	2·0
				49·8	0·9
51·5	1·0	53·5	1	52·4	3·1
58·0	0·2			60·6	2·0
61·1	0·8				
68·3	1·0	67·6	?	66·9	1·5
75·3	0·2			74·8	1·7
81·8	0·8	79·5	1	82·2	1·7
				86·2	0·9
				89·9	1·2
94·7	0·4			93·3	1·7
103·0	0·2			101·5	2·0
109·1	1·2	110·3	?	111·6	1·2
122·0	0·2			122·0	1·0
				128·7	1·4
133·2	0·6			134·6	1·4
				140·0	1·3
				151·8	1·4
				162·3	1·0
165·0	0·8	167·0	?		
				173·2	1·2
				181·2	1·2
				192·7	1·8
199·0	0·6				
				212·7	1·3
				223·2	1·1
				227·7	1·8
239·5	0·4			242·7	1·3
250·6	0·2			252·0	1·6
		257·0	2	260·9	1·4
275·6	0·6			275·0	2·0
				281·5	1·4
				289·9	0·9
				306·5	1·8
320·5	0·2 (322·2) (0·4)				
				336·3	2·0
345·5	0·2 (344·9) (0·6)				
		351·0	5		
406·8	0·4 (406·0) (0·6)				
440·7	0·6 (439·8) (0·6)				
		450·0	5		
472·6	0·2 (472·3) (0·9)				
503·6	0·4 (503·0) (0·6)	498·0	1		

a soft X-ray value. This is particularly striking in the range below 200 volts. Thomas has within this range 24 values of which nearly 15 have been obtained in the secondary electron curves. But above 200 volts the number of secondary electron inflections is much less than that of the soft X-ray values. But wherever there are secondary electron discontinuities it may be seen from Table II of Richardson and Rao (' Roy. Soc. Proc.,' A, *supra*, p. 16) that the corresponding soft X-ray inflections are the strongest in the neighbourhood, in most cases. These values, uncorrected, have been added, in brackets, for convenience.

The coincidence of so many values certainly cannot be entirely a matter of chance. We can thus say not only that inflections occur in the total electron curves but also that these inflections are related to the soft X-ray discontinuities in the manner pointed out by Richardson.*

In fig. 5 are given typical curves of total secondary emission as a function of the applied potential in the ranges 30 to 70 volts and 225 to 285 volts.

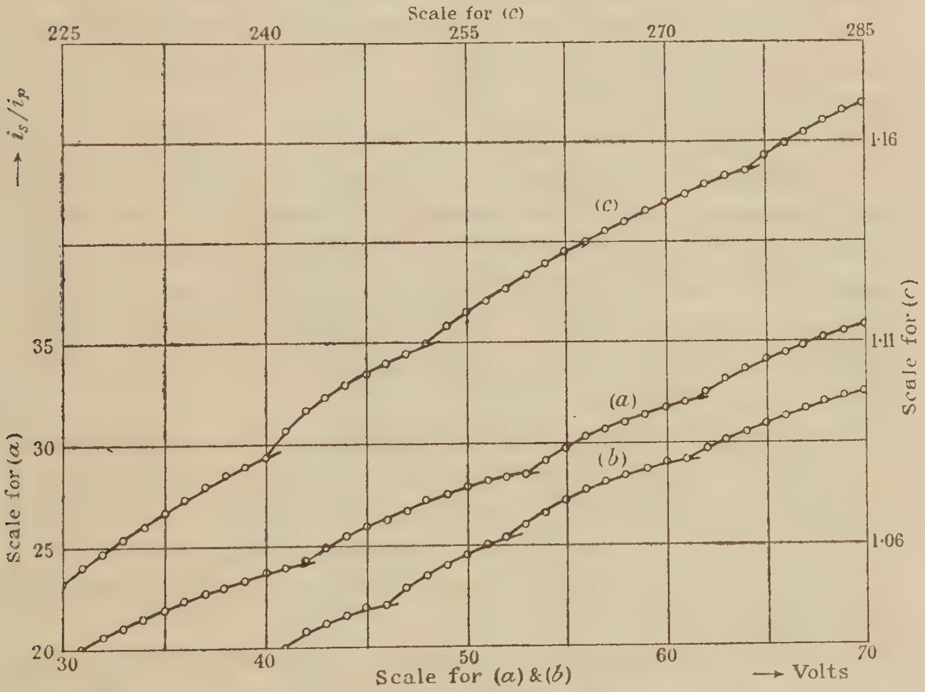

FIG. 5.—Secondary electron curves for polycrystalline nickel target. Range of potential 30 to 70 volts for curves (*a*) and (*b*) and 225 to 285 for curve (*c*). Ordinates given refer to (*a*) and (*c*). For those of (*b*) add 0·03 to those given for (*a*).

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* ' Roy. Soc. Proc.,' A, vol. 119, p. 531 (1928).

6. *Effect of Hydrogen.*

(*a*) *Total Secondary Electron Emission.*—In a recent paper Nakaya* showed the effect of bombarding the target in an atmosphere of hydrogen on the excitation of soft X-rays. He believed that the hydrogen would remove any oxide layer on the surface of the metal targets and would thus give much more steady values. An examination of this question was therefore undertaken.

A palladium tube was connected to the apparatus and the metal parts were thoroughly de-gassed. The pressure was then reduced to sticking. This means it was not more than about 10^{-7} cm. of mercury. All the taps were kept open. The palladium tube was then heated by a hydrogen jet until the pressure inside rose to about 30×10^{-3} cm. The tap was then closed immediately. In a short time the pressure outside was reduced to sticking and after about 20 minutes the tap was opened again. The pressure now fell to about 1×10^{-3} cm. Even allowing for the expansion and the consequent decrease in pressure, this value would indicate that a lot of hydrogen had been adsorbed by the target and metal parts.

This operation was repeated twice or thrice. After this, liquid air was replaced around the charcoal tube. The filaments were glowed, the metal parts heated and the target was bombarded (15 milliamps. at 540 volts) for an initial period of $1\frac{1}{2}$ or 2 hours. The bombardment was stopped, and after 5 minutes the total secondary electron current for unit primary current was determined at a known voltage. Heating was commenced and after another half-an-hour readings were taken again. This was repeated at intervals for a period of nearly 12 hours.

In fig. 6 two curves are drawn showing the variations of the secondary current per unit primary current with time of bombarding at 100 and 300 volts. It is found that as the target is bombarded the value of i_s/i_p decreases rapidly at first and then more slowly until a comparatively steady value is reached after 4 hours of bombarding. Longer bombarding, however, decreases the value gradually.

This rather peculiar behaviour of the metal surface in hydrogen may have the following explanation. Evidently there will be a large amount of hydrogen adsorbed by the surface and probably any oxide film on the metal face may be reduced when the heating takes place. As the target is bombarded the adsorbed hydrogen will be liberated but after 4 hours of bombarding a steady state seems to be attained which persists for a long time later. This seems to suggest that there are two kinds of adsorbed molecules, one kind which is loosely adsorbed and the other kind which is more firmly adsorbed. The former can be liberated by bombarding for about 4 hours under the conditions of these experiments. The other kind gets out with difficulty and more than 8 hours of more or less continuous bombarding is necessary.

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* 'Roy. Soc. Proc.,' A, vol. 124, p. 616 (1929).

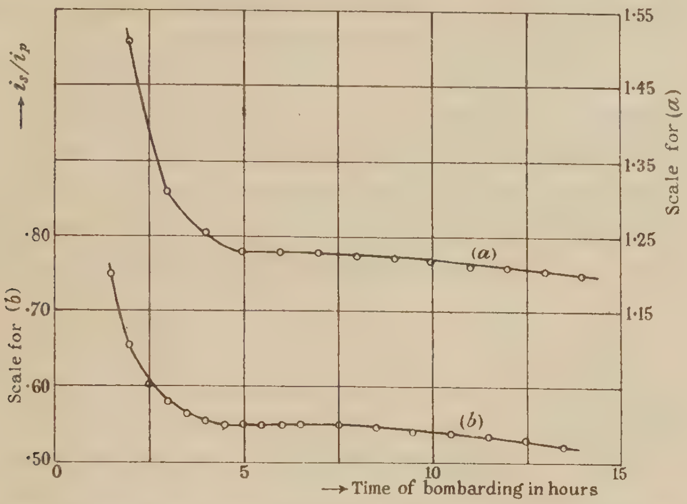

Fig. 6.—Curves showing the variation of i_s/i_p with time of bombarding after the nickel target is exposed to hydrogen for a time. (*a*) At an applied potential of 300 volts. (*b*) At an applied potential of 100 volts.

The latter kind is probably similar to the stable hydrogen molecules described by Davisson and Germer (*loc. cit.*) and Germer* in the case of the 111 face of the nickel crystal. Here the hydrogen molecule occupies a place in the middle of three nickel atoms and so gets a fairly stable position. Thus the whole surface of the target (which consists of several crystal faces) will be filled up by hydrogen molecules occupying stable positions. When all the loosely adsorbed molecules are driven out by bombarding a comparatively steady condition is reached. The value of i_s/i_p is steady corresponding to the nickel atoms on the surface interspersed with hydrogen molecules. Considerable bombarding is necessary before the stably adsorbed molecules of hydrogen are driven out, and even when this takes place it takes place slowly. This suggests that continuous bombarding does take off the stably adsorbed molecules, though the process is a very slow one.

The author has described these points at some length because of the importance of de-gassing the targets in soft X-ray and secondary electron experiments.

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* 'Bell System Tech. J.,' vol. 8, p. 591 (1929).

They show that it is difficult to de-gas the targets in a short time. Long and continuous bombarding is necessary before the more stably adsorbed molecules of gas are driven out. We can add further that this stability of adsorption seems to depend also on the nature of the metal target.

(*b*) *Influence on the Inflections.*—The nickel target was placed in an atmosphere of hydrogen as explained above and bombarded for 6 hours. If the foregoing explanation is correct the surface should now consist of stably adsorbed molecules. Total secondary emission curves were drawn in the ranges 1 to 30 volts and 400 to 460 volts. In figs. 7 and 8 curves are drawn in these ranges. In fig. 8 curves obtained in § 5 are also given for comparison.

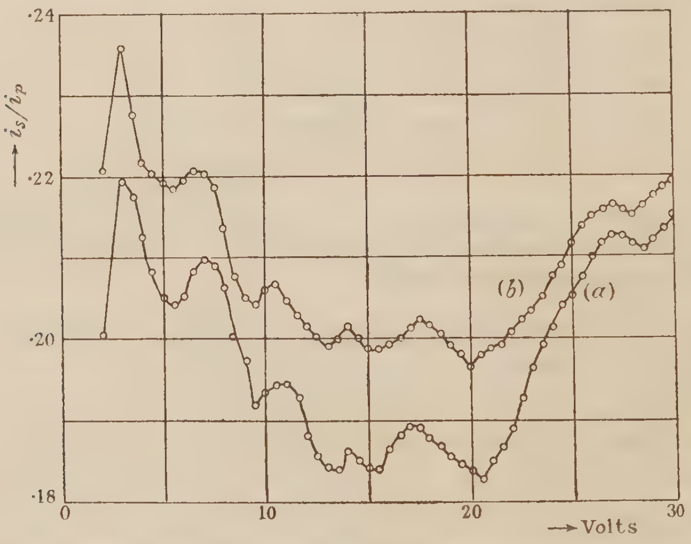

FIG. 7.—Curves between applied potential and i_s/i_p for ordinary nickel (polycrystalline) after heat treatment in an atmosphere of hydrogen. Range of potential is from 1 to 30 volts. The scale marked along the Y axis refers to curve (*a*). For the correct ordinates of curve (*b*), subtract 0·01 from the values marked.

If we compare the figures 4 and 7, it is interesting to note that in the region 1 to 30 volts besides the peaks obtained with the gas-free nickel surface there is one additional peak at 10 volts. The peak at 14 volts has become stronger. It is not improbable that these peaks are due to the extra net of hydrogen molecules on some of the principal crystal faces on the polycrystalline target.

In the region, however, of 400 to 460 volts, there was practically no change in the shape of the curves, though the absolute intensity was about 8 per cent. higher. The inflections at 408 and 448 volts were just detected, their intensities being much lower than in the case of fresh surfaces.

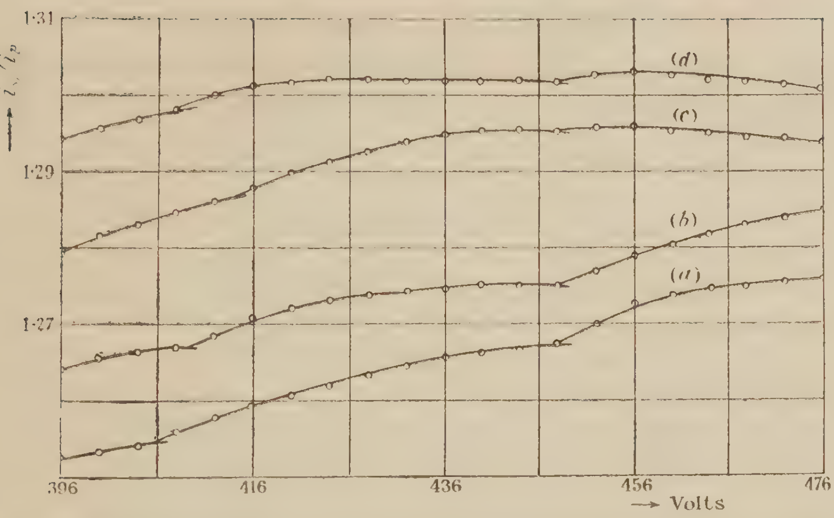

FIG. 8.—Curves (*a*) and (*b*) refer to ordinary nickel target. Curves (*c*) and (*d*) are after heat treatment in hydrogen. Ordinates given refer to curves (*a*) and (*c*). For (*b*) and (*d*) subtract 0·01.

No further investigations at different ranges of potential were made as it was not expected that they would lead to anything further of a very novel character.

7. *Effect of Heating the Target.*

Most of the readings at ordinary temperatures were taken just after bombarding the metal surface, so that it was fresh and well de-gassed. Readings were taken also keeping the target at 550° C.

To prevent electrons from the filament F_2 from interfering with the experiments, this filament was maintained at about 12 volts higher than the target. Even then it was found that the current reaching the shield C from the cylinder was about $1 \cdot 2 \times 10^{-7}$ amp. This appears to be too much to be the ordinary thermionic current from the hot nickel cylinder. It is probable that this current is due to electrons from the filament F_2 being reflected from the cylinder on to the shield. Whatever the cause may be it was found, luckily, that this current had a constant value and was merely added on to the secondary current.

Total secondary electron curves were drawn for the target at 550° C. So far as the inflections were concerned there was no change in their values. Nor did any inflections disappear in the manner observed by Krefft. However, it is possible that the comparatively low temperature to which the target was heated in these experiments was responsible for the absence of this effect.

8. *Total Secondary Electron Curve.*

In fig. 9, curve (*a*) shows the variation of the total secondary emission per unit primary current in the range from 30 to 550 volts. It is found that at first i_s/i_p increases almost linearly from 30 to about 225 volts. After this the curve gradually bends round and becomes horizontal at about 500 volts. For comparison the curve of Petry has also been drawn in the same range. The shapes of the curves are quite similar. At lower potentials Petry's values are much higher.

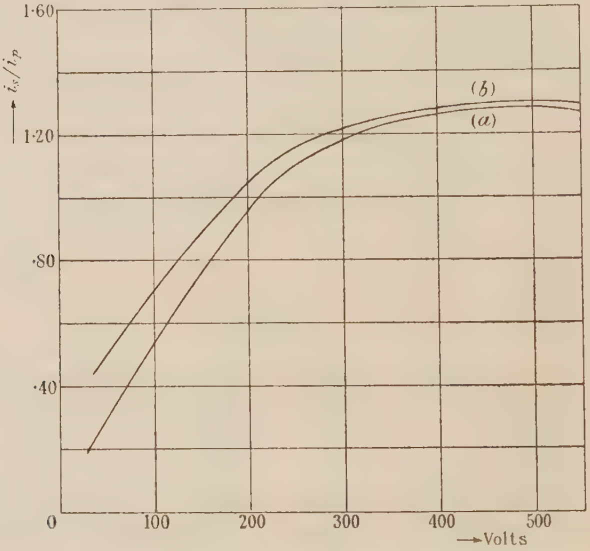

FIG. 9.—Total secondary electron curves for the nickel polycrystalline target in the range below 550 volts. (*a*) Obtained by the author. (*b*) Obtained by Petry.

The reason why the curve bends round and at higher potentials even goes down seems to be still obscure. In this connection it is interesting to note that Hyatt and Smith* get similar total secondary electron curves for molybdenum, using a different method of investigation.

Finally, I take this opportunity of thanking Prof. O. W. Richardson, F.R.S., for his guidance and help and for the very valuable suggestions made by him during the course of the work.

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* 'Phys. Rev.,' vol. 32, p. 929 (1928).

Total Secondary Electron Emission from a Single Crystal Face of Nickel.

By S. Ramachandra Rao, M.A., King's College, London.

(Communicated by O. W. Richardson, F.R.S.—Received March 1, 1930.)

1. *Introduction.*

In an accompanying paper, secondary electron experiments on ordinary nickel are described. These were conducted mainly to study the conditions of secondary electron emission and to find how far the experimental results of Petry on a polycrystalline nickel target could be reproduced. It was found that a large number of inflections were obtained some of which coincided with Petry's values. Most of these inflections had corresponding values in Thomas's results for soft X-rays from nickel. In this paper, the results of experiments on total secondary electron emission from the 100 face of a nickel crystal are given.

2. *Experimental Details.*

The single crystal used was the same as the one used for X-ray work by Richardson and Rao.[*] It was placed in the same apparatus and in the same position as the polycrystalline target in the preceding experiments on secondary electron emission. Care was taken not to heat the crystal to temperatures greater than 1000° K. A large number of secondary electron curves were drawn and the results are given below.

3. *Results.*

(*a*) *Peaks in the Range* 1 *to* 30 *volts.*—In this range only two peaks were obtained, one at 3 volts and the other at 14·5 volts. No other peaks were obtained. This is interesting and goes strongly to support the idea that the peaks with a polycrystalline target are due to reflection or diffraction of electrons from the crystal faces of different orientations on the surface.

Typical curves in this range are shown in fig. 1. The smoothness of the curves can be compared with the irregular nature of the curves in fig. 4 of the paper dealing with polycrystalline nickel.

(*b*) *Inflections in the Range* 30 *to* 550 *volts.*—In Table I are given the inflections obtained in the secondary electron curves for the 100 face of the nickel crystal.

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[*] 'Roy. Soc. Proc.,' A, *supra*, p. 37.

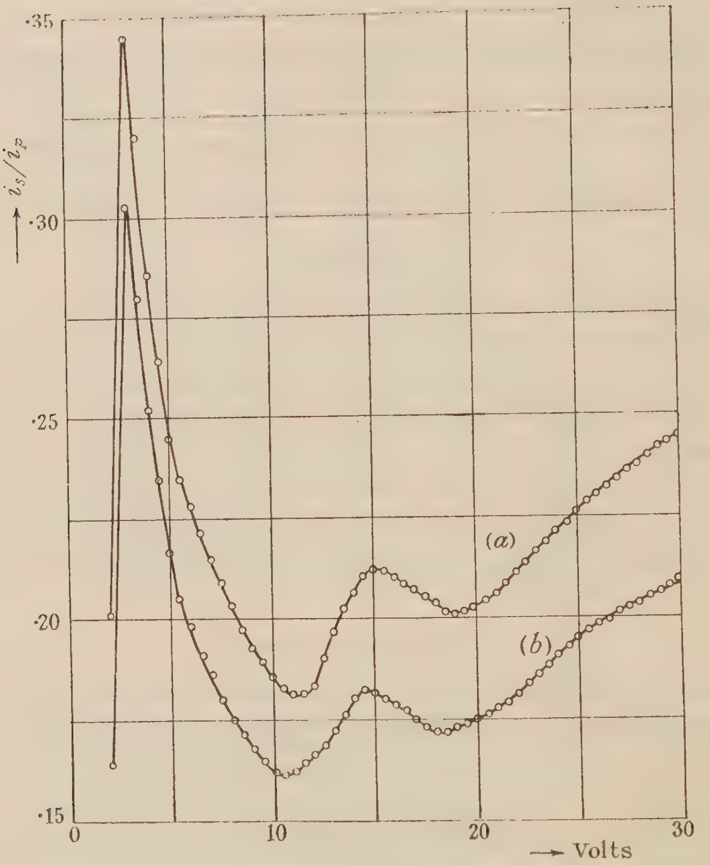

Fig. 1.—Curves between applied potential and i_s/i_p for Ni crystal in the range 1 to 30 volts. The scale marked along the Y axis is for curve (*b*). For (*a*) subtract 0·01.

For comparison similar values obtained for soft X-ray excitation from the same face are also given. Further, the secondary electron discontinuities got by the author and by Petry for polycrystalline nickel targets and the nearest soft X-ray inflections of Thomas are also given. In all cases the values are uncorrected for the work function.

A comparison of the different values is very interesting. For the crystal there are 18 secondary electron discontinuities. The following points are noted:—

(1) It was mentioned in the paper dealing with the soft X-ray experiments for the crystal that these were sensitive only in the range above 50 volts. Above this value there are 15 discontinuities in the secondary emission and 11 inflections in soft X-ray excitation. All the 11 values

Table I.

Soft X-ray, Ni crystal, face 100. R. and R.		Sec. elec., Ni crystal, face 100. Author.		Sec. elec., Ni polycrystalline. Author.		Sec. elec., Ni polycrystalline. Petry.		Soft X-ray, Ni polycrystalline. Thomas.	
Volts.	Intensity.	Volts.	Intensity.	Volts.	Intensity.	Volts.	Intensity.	Volts.	Intensity.
Below range of sensitivity of apparatus				30·8	1·2	30·0	2		
		35·1	0·2					34·8	1·4
		41·4	0·5	39·9	1·0	43·2	3	39·7	1·5
				45·7	0·6			—	—
		49·2	0·6	51·5	1·0	53·5	1	49·8	0·9
58·3	1·9	57·1	1·0	58·0	0·2			60·6	2·0
				61·1	0·8				
67·1	1·3	66·6	0·9	68·3	1·0	67·6	(?)	66·9	1·5
				75·3	0·2			—	—
		78·8	0·5	81·8	0·8	79·5	1	82·2	1·7
								—	—
89·4	0·5	88·9	0·5					89·9	1·2
				94·7	0·4			—	—
101·6	1·4	99·7	1·0	103·0	0·2			101·5	2·0
111·2	1·1	109·6	1·0	109·1	1·2	110·3	(?)	111·6	1·2
124·1	0·4	124·2	0·8	122·0	0·2			122·0	1·0
				133·2	0·6			—	—
								—	—
139·9	0·4	137·5	0·5					140·0	1·3
151·0	0·4	151·5	0·3					—	—
				165·0	0·8	167·0	(?)	—	—
175·0	0·3	171·5	0·4					173·2	1·2
181·1	0·3	181·5	0·2					181·2	1·2
		195·5	0·2					192·7	1·8
				199·0	0·6				
212·8	0·3	211·4	0·4					212·7	1·3
								—	—
		226·6	0·2					227·7	1·8
				239·5	0·4			—	—
		244·1	0·2					242·7	1·3
								—	—

Note.—In the values of Thomas in the last column the dash indicates that a value has not been given.

agree with those in the secondary emission. There are four values, 78·8, 195·5, 226·6 and 244·1 that are present in the secondary electron curves and not in the soft X-ray curves. Of these, those at 195·5, 226·6 and 244·1 volts are very weak and possibly could not have been obtained in the soft X-ray work. The other values agree very satisfactorily with secondary electron discontinuities. This is significant when one notes that the observations were made with different types of apparatus and conditions.

(2) Even in intensities there may be traced a resemblance. It will be noted that the soft X-ray inflections at 58·3, 67·1, 101·6 and 111·2 are very strong. In the same manner the corresponding values in the secondary emission curves are also strong.

(3) Comparing the secondary electron discontinuities from the crystal face and the polycrystalline target, a coincidence can be traced between the values up to 125 volts. But above this there is no longer any coincidence. This probably indicates that in the polycrystalline target, the representation of the 100 face and the conditions were such that values above 125 volts could not occur.

(4) Comparing the secondary electron discontinuities for the crystal with the soft X-ray inflections of Thomas for the polycrystalline target, it is found that there is good coincidence between the sets of values. According to Thomas's measurements there are in all 35 inflections in the range 30 to 340 volts, and of these 18 occur in the secondary electron curves for the crystal.

These results are discussed more fully below.

In fig. 2 are given secondary electron curves in the ranges 50 to 125 volts.

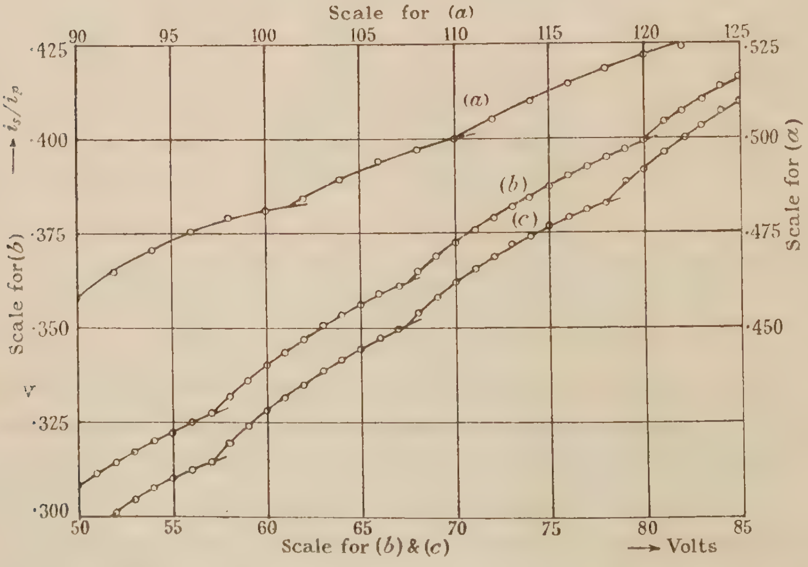

FIG. 2.—Secondary electron curves for the nickel crystal face 100. Range of potential for curves (*b*) and (*c*) 50 to 85 volts and for curve (*a*) 90 to 125 volts. Ordinates given refer to curves (*a*) and (*b*). For those of (*c*) subtract 0·01 from those of (*b*).

4. *Total Secondary Electron Curve.*

In fig. 3 is given the total secondary electron curve in the whole range from 30 to 550 volts. For comparison the curve for the polycrystalline target is also drawn. The following points are interesting :—

(1) At potentials below 60 volts the two curves are nearly coincident.

(2) Above 60 volts though the general shape is similar, there is a very great difference in absolute values.

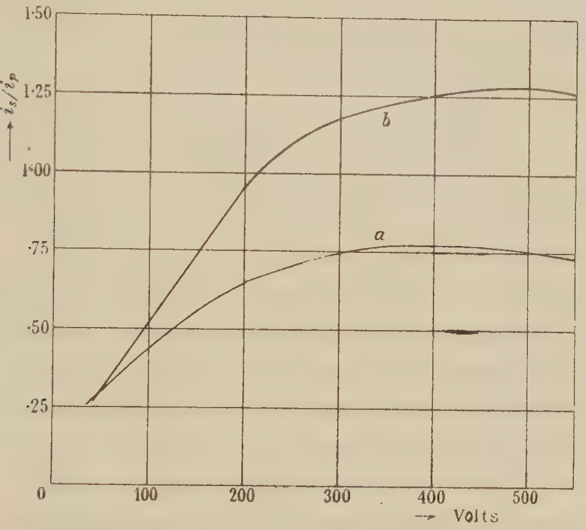

FIG. 3.—Total secondary electron curves in the range below 550 volts. *a*, for the nickel crystal face 100. *b*, for the nickel polycrystalline target face.

(3) Whereas the maximum value obtained for the polycrystalline target (about 1·28) occurs at about 500 volts, the maximum value for the crystal face (about 0·76) occurs at about 400 volts.

(4) After the maximum value is obtained, the value decreases very gradually in both cases.

As was mentioned at the end of the paper dealing with polycrystalline nickel, the causes for this peculiar behaviour are obscure. Work with other nickel crystal faces of different orientations may throw some light on the matter.

5. *Discussion.*

These experiments show that there is a very good coincidence between the soft X-ray inflections from the 100 face of the nickel crystal and the secondary electron discontinuities from the same face. This indicates that when an electron beam is incident on the crystal face, as the applied potential is increased, at every potential where there is an increased excitation of soft X-radiation, there is correspondingly an increase in the secondary electron emission or vice versa.

Recently Farnsworth* has obtained several inflections in the total secondary electron curve in the range 10·5 to 250 volts by using a copper crystal of face 100. He has shown that these inflections are due to Davisson and Germer electron scattering. It thus appears that at those potentials where the secondary electron emission increases because of selective scattering, there is an increase in the soft X-radiation also. We are thus led to the important and interesting result, that at the potential at which there is an intense scattering of electrons according to the Davisson and Germer effect, there is correspondingly an increased intensity of soft X-radiation.

It seems difficult at the present state of our knowledge of electron waves and the actual mechanism of the interaction of such waves with atoms in crystal array to justify this deduction on any satisfactory basis. But it appears probable that the conditions which give rise to large scattering of electron waves are also such as to cause an increased intensity of soft X-radiation.

A part of this increased soft X-radiation will act photoelectrically on the target itself and give rise to a larger amount of low velocity electrons in the manner pointed out by Richardson.†

If the soft X-ray excitation is connected with the effect of Davisson and Germer in the manner explained above, then we get a natural explanation of the soft X-ray inflections. The polycrystalline target consists of a large number of crystal faces of different orientations, the more simple ones like 100, 110 and 111 having a greater probability of occurrence than the higher ones. Each orientation gives rise to certain inflections as explained above and thus different orientations may cause the large number of values obtained with the polycrystalline target. The 100 face alone seems to be responsible for 18 out of 36 inflections in the range 30 to 340 volts.

The subsidiary observations made with polycrystalline targets like the intensity variations with the heat treatment of the target, seem to justify the explanation given above.

It is a pleasure and a privilege to thank Prof. O. W. Richardson for his continued interest and guidance. I desire to thank also Dr. H. H. Potter, of Bristol University, for the nickel crystal which has made these experiments possible.

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* 'Nature,' vol. 123, p. 941 (1929); 'Phys. Rev.,' vol. 34, p. 679 (1929).

† 'Roy. Soc. Proc.,' A, vol. 119, p. 531 (1928).

The Emission of Secondary Electrons and the Excitation of Soft X-Rays.

By O. W. Richardson, F.R.S., Yarrow Research Professor of the Royal Society.

(Received March 15, 1930.)

As a result particularly of experiments carried out by Miss Andrewes,* Mr. Ramachandra Rao†‡ and myself*† at King's College and by Dr. Rudberg§ in Stockholm, we now have much more information about these phenomena than we had when I|| discussed this question two years ago. The experiments of Whiddington¶ as well as of Rudberg§ have removed much of the vagueness which was then necessary as to the nature of the first process which occurs when an electron strikes a solid. It is evidently either reflected without loss of energy, as in Davisson's experiments, or it undergoes an inelastic collision of such a kind that it loses a substantial amount of energy. This is shown by the well-marked minimum in the energy distribution curve for the reflected and secondary electrons between the peak corresponding to the Davisson effect and lower energy values. In fact in important cases the density at this minimum is practically zero. This shows that in such cases there is no appreciable number of secondary electrons which have come back as a result of encounters with free electrons; since this process would give rise to a smooth and continuous distribution of velocities which should have an appreciable density at the place where the minimum occurs.

The velocity distribution curves for the secondary electrons show, in addition to the two already mentioned, a third group having a low average energy. This group is closely connected with the group which has undergone inelastic collisions, since both groups are almost absent when the energy of the primary electrons is low. The electrons which form this group are to be regarded as the true secondary electrons originating in some way as a result of the excitation accompanying the inelastic collisions. This is very definitely supported

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* 'Roy. Soc. Proc.,' A, *supra*, p. 1.

† 'Roy. Soc. Proc.,' A, *supra*, pp. 16, 37.

‡ 'Roy. Soc. Proc.,' A, *supra*, pp. 41, 57.

§ 'K. Svensk. Vetensk. Handl.,' vol. 7, p. 1 (1929); 'Roy. Soc. Proc.,' A, vol. 127, p. 111 (1930).

|| 'Roy. Soc. Proc.,' A, vol. 119, p. 531 (1928).

¶ 'Leeds Phil. Lit. Soc. Proc.,' vol. 1, p. 162 (1927); p. 242 (1928).

by the fact that the energy loss in the inelastic collisions corresponds to definite level differences which are independent of the energy of the exciting electrons and at the same time the energy distribution in this third group is very insensitive to changes in the primary voltage. It is, in fact, very similar to the energy distribution among the photoelectrons of low energy which are generated when the soft X-rays which accompany these electron emissions fall on a metal plate. This similarity suggests that these photoelectrons and the third group of secondary electrons originate in a common mechanism or at least in mechanisms of very similar type. This is indeed required by the fact that the total secondary electron emission, *i.e.*, the sum of the three groups, and the X-ray emission both show a series of discontinuous increases at the same primary voltage. These discontinuities are very numerous and it is now abundantly clear that the great majority of them have nothing directly to do with the Bohr levels which govern the structure of the atoms of the bodies concerned.

I think now that all the established facts in this domain can be harmonised by means of a fairly simple picture which has no immediate contact with the Bohr picture of atomic structure but which is not at all inconsistent, so far as I am able to judge, with our present knowledge of the structure of crystals. It is now well established that the structure of molecules is in general quite different from that of the component atoms and in a crystal this process is carried a stage further. In metallic crystals there are, for example, the free electrons which give rise to electrical conductivity and which have no counterpart in the structure of the constituent atoms. In crystals generally I assume that there are also other electrons which are not free and which do not form part of the atomic pictures. In order to talk about these I shall call them *structure* electrons. I believe that there is very strong evidence that such electrons play a fundamental rôle in the phenomena of secondary electron emission and the generation of soft X-rays.

According to this picture when an electron reaches a crystal face it is either diffracted by the crystal grating or it reacts with one of the structure electrons. The only orthodox way in which it can react with this is to raise the energy of the structure electron from its normal state to some excited state. To do this it must lose at least as much energy as is equivalent to the level difference between the ground state and the next higher state. This at once accounts for the existence of a minimum which may be as low as zero between the peak which corresponds to diffraction or reflection and the groups of electrons with somewhat lower velocities in the distribution curves. Furthermore such an interaction will not occur unless the impinging electron has an amount of energy in excess of this level difference and it is well established that there is little except direct reflection when the energy of the primary electrons is low. These interactions also must set in with some suddenness as the voltage is raised; since it is clear from Rudberg's distribution curves for carbon and lithium that with both these substances there is a very large jump in the amount of scattered electrons somewhere in the range between 48 and 70 volts for the primaries.

On this view we expect a sudden change in the secondary electron emission to set in at each of the levels of the structure electrons so that it furnishes a natural explanation of the discontinuous changes in the total secondary emission as the primary voltage is continuously raised.

There are several alternatives which might be adopted to account for the origin of the true secondary electrons, the third group with low average energy. After the structure electrons have been excited the only thing they can do of themselves is to get rid of their excess energy by radiation. This would, of course, be quantised but would not necessarily be the $h\nu$ equivalent of the $\frac{1}{2}mv^2$ taken from the primary electrons since there might be alternative routes back to the ground level; for these, however, the total $\Sigma h\nu$ would be $= \frac{1}{2}mv^2$. Part of this radiation would then act photoelectrically causing the ejection of the secondary electrons and some of it would escape and so contribute to the soft X-rays which are generated at the same time. The occurrence of these processes, which seem to follow inevitably from the premises, at once furnishes an explanation of the similarity in the velocity distribution among the true secondary electrons with that among the low velocity group generated by the soft X-rays, *i.e.*, the group which does not appear to be connected with the Bohr levels. It also accounts for the agreement between the secondary electron and the soft X-ray discontinuities. It is also reasonable to anticipate that the upper levels of the structure electrons will be more crowded together than the lowest; so that these processes would be expected to give rise to a group of low velocity electrons, such as is found, in which the effects of the discrete levels of the structure electrons are largely lost.

Broadly speaking, this bears considerable resemblance to the view to which I was led in my former paper; but it has to face some difficulties and whilst I feel that these processes must occur and account for some part of the true secondary electron emission it is far from certain that they account for the whole of it. The central difficulty is the low efficiency of X-ray emission which was discussed in the former paper. The processes of energy conversion into

X-rays in the solid now under consideration have a high efficiency so that to account for a low efficiency of X-ray generation it is necessary, as in that paper, to endow the X-rays with a greatly enhanced (of the order of 10^6 times) coefficient of absorption where they are generated. At first sight the structure electrons seem to provide a mechanism for this. For the most part the soft X-rays will consist of quanta arising from the transference of electrons between upper levels, not down to the ground level, and there is no existing mechanism for the absorption of such radiation quanta in a substance not provided with a set of upper states such as it has when it is subject to electron bombardment. The average absorption coefficient of the radiation might well be of a higher order in a specimen undergoing electron bombardment. However, this idea can be tested by existing experimental data. If there is a special absorption *arising from this cause* it should be less for a specimen bombarded with a low than for one bombarded with a high electron current density. From this it should result that the X-ray generation efficiency, as measured by i_p/i_t for example in the type of apparatus we use, should under otherwise similar conditions increase as the thermionic current i_t is diminished. Well, our experiments showed some increase in i_p/i_t as i_t was diminished but it was nothing much, at most about 20 per cent., as i_t dropped from about 4 to about 2 milliamps. This rate of increase was increasing fastest at the lower values of i_t but on the other hand Nakaya found it to be constant, within his error of measurement (1·0 per cent.) with the still lower range of values of i_t from 8 to 60 microamperes. In fact the straightforward inference from Nakaya's results is that if the special absorption is to be accounted for after this fashion, then only a quite small fraction of the true secondary electrons can be generated in this way. It is, however, not excluded that the special absorption might arise from the operation of some entirely different principle such as would also correlate the other phenomena referred to in my former discussion.

The second alternative for the generation of the true secondary electrons is to suppose that the excited structure electrons lose their energy by electron impact. In the case of metallic conductors a mechanism for this is provided by the free electrons which will react with the excited structure electrons and take up the energy of these in the form of kinetic energy by collisions of the second kind, as they are called. Having acquired this additional energy those electrons which are favourably situated will then be able to escape from the surface as a group of secondary electrons. As the free electrons may have any assigned energy, although for practical purposes this must with a Sommerfeld distribution lie below a certain limit which, however, is rather high, and as the energy of an electron which originates with a given velocity may be affected by other encounters before escaping, we should expect the emergent group of secondary electrons to preserve little or no evidence in their energy distribution of the discrete energy levels which have been attributed to the structure electrons. There is some evidence that this mechanism will not account for the whole of the true secondary electron emission. If it did one might expect that such emission would be of a higher order of magnitude for the very good metallic conductors than for the oxides; but the experimental evidence does not indicate that there is any very extraordinary difference between them. Again, if this "quenching" of the excited states by free electrons is all important it would be natural to expect a much higher efficiency of generation of soft X-rays when the quenching is greatly reduced. Thus when the surface of a metal is oxidised to an appreciable extent one would expect it to generate many more soft X-rays under given conditions, but L. P. Davies* found no very striking difference between the soft X-ray emission from clean and oxidised wires. It is probable that both the alternatives I have discussed are operative in varying degrees under different circumstances, but it is well to remember that unless the second, or some other, alternative can be made to yield practically the whole of the secondary electrons we still have the difficulty of the abnormal local absorbability for the X-rays required by the first alternative. I feel that this is an important issue and further experiment ought to be directed towards trying to settle it.

There is a third alternative which has been discussed by Rudberg who suggests that the greater part of the low energy secondary electrons result from the direct action of the primary electrons on the great number of free electrons in the substance. I find this very difficult to reconcile with his own experimental evidence, particularly with the absence of such low energy secondary electrons for rather low velocities of the primary and with the zero density which occurs in many cases just below the total reflection peak. If these secondary electrons arise from such direct action they ought to appear at much lower primary voltages than they do and their formation would rob the primary electrons of a continuous distribution of small amounts of energy which would have the effect of filling up the gap near the peak.

There is a variation of this alternative for which there is more to be said. Since the primary electrons are moving inwards they might be rather ineffective in knocking free (*i.e.*, conduction) electrons outwards, but the electrons which have undergone inelastic collisions would not suffer from this disability. It might, therefore, be argued that the slow group arise from the interaction of the fast returning electrons with the free electrons. This is difficult to distinguish in its effects from the first two alternatives and especially from the second. All three make the slow group appear with the group of electrons which have lost relatively little energy, in fact, they all involve a close correlation between these two groups. As with the second we should expect a feeble development of the low velocity group with poor conductors but I know of no evidence bearing on this point. The alternative under consideration does not afford any obvious way of avoiding the high local absorption difficulty, and it does not explain why the velocity distribution in the slow group is almost independent of the voltage of the primary electrons and is so very similar to that in the slow group of photoelectrons generated by the accompanying soft X-rays ; so that it seems to offer no advantages over either of the first two alternatives.

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* 'Roy. Soc. Proc.,' A, vol. 124, p. 268 (1929).

It does not seem possible at the present stage to apportion the effects decisively between these possible mechanisms, but it is sufficient for the purpose of this discussion to know that there is at least one mechanism which is capable of generating the group of slow electrons with such properties as they actually are found to possess.

On the present view the soft X-rays are generated largely by the normal return of the excited structure electrons to lower states and ultimately to the ground state, spontaneously, without the intervention of other electrons. The low yield is to be accounted for, as already stated, either by a local abnormally high absorption coefficient or by quenching or possibly by both mechanisms. In addition there is evidence both from the soft X-ray excitation potential data, and also from Rudberg's analysis of the velocity distribution among the photoelectrons generated by the soft X-rays, of such rays coming from the excitation of the Bohr levels of the atoms. There is, however, little or no evidence that this group of X-rays plays anything but an insignificant part in the generation of the secondary electrons during electron impact and there does not seem to be any need to postulate for them either any very abnormal local absorption coefficient or alternatively of the extinction of the corresponding excited states by collisions. This last supposition would at any rate seem reasonable enough as the corresponding levels would generally lie too deep down in the atoms for the free electrons to reach.

I shall now consider what indications we have as to the nature of the levels occupied by the structure electrons. On the view I am taking there can be little doubt that the levels found by Rudberg in his analysis of the energy loss of the groups of electrons reflected with high energy are examples of them.

In this case at least there seems to be no possibility of confusion with electron wave diffraction effects since he finds that the shape and width of the gap from the high voltage peak, caused by reflection without energy loss, to the next maximum, is independent of bombarding voltage, orientation of target and direction of scattering. Whilst the velocity analysis method is excellent for disentangling the different effects involved, it may prove incapable of being developed to a very high degree of refinement and, in the present instance, only yields information about a few of the lowest levels. It may or may not be significant that in the case of the metals investigated by Rudberg (Cu, Ag, Au and Pt) all the level differences found are capable of being represented by $mL_1 + nL_2$, where L_1 and L_2 are the two lowest level differences and m and n are integers whose sum never exceeds 5. The precise physical significance to be attributed to the maxima in the curves seems somewhat doubtful. It would seem more natural to fix the levels so as to correspond to points on the curves where discontinuous changes of slope are detectable.

Turning in another direction, I think that most of the discontinuous changes of slope when either the photoelectric yield of soft X-rays (i_p/i_t) on the one hand, or the total yield of secondary electrons ($i_{\text{sec.}}/i_{\text{primary}}$) on the other, is plotted against the voltage applied to the primary electrons, are to be attributed to the excitation of the different levels of the structure electrons. There is a substantial agreement between the results given by these two methods (secondary electrons and soft X-rays) when the data are treated in a corresponding manner in both cases. These methods do not exclude the possibility of effects arising from electron diffraction phenomena. On the other hand, they are the only methods available at present which appear to yield any information about the higher excitation levels involved. As to the structure of these higher levels Dr. Chalklin and I* found that a great part of the complicated soft X-ray data given by the metals of the iron group and copper could be co-ordinated into a scheme of levels of a Rydberg type such as would arise from transitions between a limited number of atomic levels and series of excited levels of the type familiar in line spectroscopy. Whilst this matter is still undecided, and it seems improbable that all the regularities which we observed can be merely accidents, the recent data which we have obtained in the laboratory by the investigation of the discontinuities got by the bombardment of single faces of crystals point in a different direction. A single crystal face should, in theory at any rate, give rise to results which are capable of a simpler interpretation than those from a polycrystalline surface. Using the

* 'Roy. Soc. Proc.,' A, vol. 119, p. 60 (1928).

data given by the experiments with crystals as a starting-point I have been led to the conclusion that these structure electron levels are built up in a very similar way to that of the levels to which we attribute the source of a system of vibration bands in molecular spectra. Two examples, one for carbon and the other for aluminium, showing how all, or practically all, the data can be co-ordinated in a numerical scheme of this type are given in the paper by Miss Andrewes and myself. Another example is shown in the figure. In this figure I have plotted all the critical potentials found by Ramachandra Rao in the secondary electron emission from the 100 face of a nickel crystal, as ordinates, against consecutive whole numbers, as abscissæ. The points fall almost, but not quite, on a continuous curve. They do, however, certainly fall on the three curves drawn within the limits of error of observation. I have, therefore, arranged the critical potentials belonging to these three sections with the resulting horizontal and vertical differences in Table I. It will be

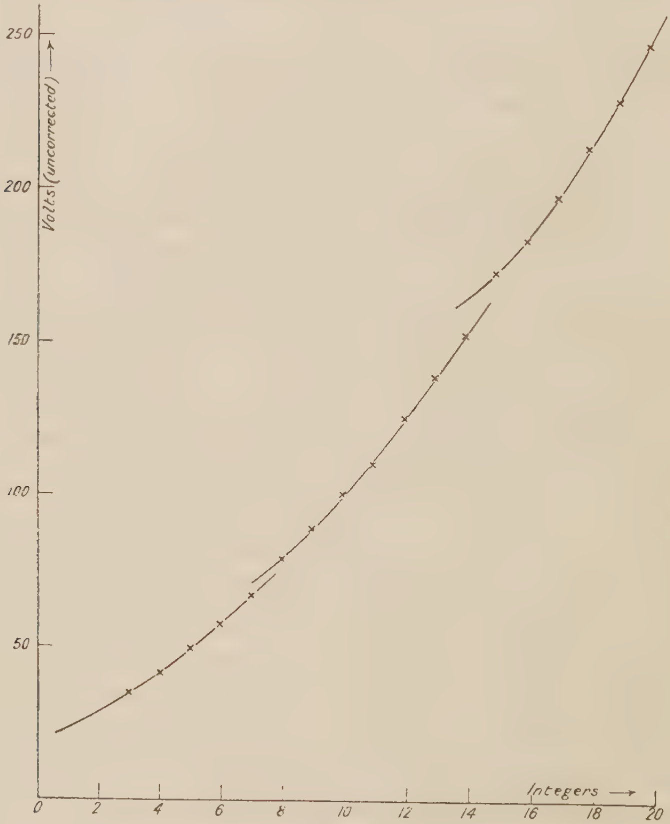

Table I.

Critical potential	171·5 (0·4)	181·5 (0·2)	195·5 (0·2)	211·4 (0·4)	226·6 (0·2)	244·1 (0·2)	
Horizontal diff.	10·0	14·0	15·9	15·2	17·5		
Vertical diff.	92·7	92·4	95·8	101·8	102·4	106·6	
Critical potential	78·8 (0·5)	88·9 (0·5)	99·7 (1·0)	109·6 (1·0)	124·2 (0·8)	137·5 (0·5)	151·5 (0·3)
Horizontal diff.	10·1	10·8	9·9	14·6	12·3	14·0	
Vertical diff.			64·6	68·2	75·0	80·4	84·9
Critical potential			35·1 (0·2)	41·4 (0·5)	49·2 (0·6)	57·1 (1·0)	66·6 (0·9)
Horizontal diff.			6·3	7·8	7·9	9·5	

seen that all the differences increase slowly but regularly in going from left to right, that is, towards higher quantum numbers. Any irregularities which occur are only such as should arise from the inaccuracies which are present in the experimental data. It is important to note that this table as well as the curves in fig. 1 include *every* discontinuity which Ramachandra Rao could find, and also that none were present in the range from 244 to 340 volts although it was examined very carefully. Furthermore, this arrangement gives a regularity to the estimated intensities of the discontinuities. These are given in brackets after each critical potential and it will be seen that they first increase and then diminish in passing from left to right in each row. That this is not obvious from the top row is probably of no significance since the corresponding breaks are all so weak that it is difficult to estimate a number for their respective intensities.

It remains to consider whether the scheme which has been outlined is reasonable from a theoretical standpoint, and involves reasonable magnitudes for the physical quantities concerned. I think it can be shown to satisfy these requirements. Let x, y, z be Cartesian co-ordinates representing the displacement of a structure electron from its equilibrium position if it has one, and from its average position if it has not, then the kinetic energy of this electron is $T = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$. If the co-ordinate axes are properly chosen with reference to the axes of crystal symmetry it is pretty certain that in a considerable number of cases the potential energy of this electron can be written in the form

$$W = f(x) + g(y) + h(z), \tag{1}$$

where f is a function only of x, g of y and h of z. Since the equations of free motion are given by

$$\frac{\partial}{\partial t}\left(\frac{\partial T}{\partial \dot{q}}\right) - \frac{\partial T}{\partial q} + \frac{\partial W}{\partial q} = 0,\ q = x,\ y \text{ or } z, \tag{2}$$

they are

$$\left.\begin{aligned} m\ddot{x} + f'(x) &= 0 \\ m\ddot{y} + g'(y) &= 0 \\ m\ddot{z} + h'(z) &= 0 \end{aligned}\right\}. \qquad (3)$$

If the structure electron has a position of static equilibrium then for this position $\frac{\partial W}{\partial q} = 0$ when $T = 0$ and the first term in f, g or h is the quadratic term. It is probable that for fairly small oscillations this will be the dominant term, so that to a first approximation we can put

$$f(x) = \tfrac{1}{2}ax^2, \quad g(y) = \tfrac{1}{2}by^2, \quad h(z) = \tfrac{1}{2}cz^2. \qquad (4)$$

If these are substituted in (3) the equations become the equations of a three-dimensional Planck oscillator and its proper values are

$$E_x + E_y + E_z = (n_x + \tfrac{1}{2})\, h\nu_x + (n_y + \tfrac{1}{2})\, h\nu_y + (n_z + \tfrac{1}{2}) h\nu_z \qquad (5)$$

where n_x, n_y, n_z are integers and

$$\nu_x = \frac{1}{2\pi}\sqrt{\frac{a}{m}}, \quad \nu_y = \frac{1}{2\pi}\sqrt{\frac{b}{m}}, \quad \nu_z = \frac{1}{2\pi}\sqrt{\frac{c}{m}}. \qquad (6)$$

Equations (5) would give a triple set of equally spaced levels. In many cases considerations of symmetry will reduce this to a double set and even to a single set. However, the reduction to a single set is hardly likely to be of importance in the present phenomena which are superficial. The presence of the surface will generally ensure that the symmetry in one direction differs from that in the others. The equal spacing of the levels given by equations (5) depends fundamentally on the quadratic form of the potential energy function. We know from the theory and facts of molecular vibration spectra that the effect of the higher terms in this function is to make the spacing change in a fairly uniform way as we pass along a given set of levels. These are precisely the properties which we have found empirically for the levels representing the excitation potentials of soft X-ray and secondary electron emission.

From what is known about crystal structure we expect that a large proportion of the potential energy of a structure electron will be derived from the field of the two nearest atoms, and that the general magnitude of the force on this electron will be given by disregarding all other objects except these two atoms. I assume that the force exerted by them is that coming from two nuclei with an effective charge ze, z being an atomic number suitably reduced by the screening of the inner electronic levels. On this hypothesis the coefficient a is given by

$$a = 4ze^2/x^3_0, \tag{7}$$

where $2x_0$ is the distance between the two atoms or, in other words, the lattice constant of the crystal. Substituting this in (6) and putting as sufficiently correct $e = 4 \cdot 8 \times 10^{-10}$, $m = 9 \times 10^{-28}$, $x_0 = 10^{-8}$ and dividing by 8100 to turn the level spacing from frequencies to volts, we find that the order of magnitude of the level spacing is

$$21 \cdot 3 \sqrt{z} \text{ volts}. \tag{8}$$

It can hardly be a coincidence that all the levels which have been obtained empirically and without any assistance from this theory all range around what would be expected from this formula.

Carbon is the only element for which at present we have both an analysis of the soft X-ray or secondary electron inflection data based on observation of a single crystal face and also a velocity distribution analysis of the secondary electrons. In this case the two sets of phenomena give a mutual quantitative confirmation. The analysis of the carbon data given by Miss Andrewes and myself shows levels at about 9, 13·5, 53·4 and 63·0 volts above the ground level. On the other hand, the figures (fig. 48) on p. 128 of Rudberg's dissertation* all show two groups of fast secondary electrons which have lost 4·5, 9 or 18 volts energy so far as I can judge them. However they are interpreted, the intervals are quite similar to the two lower of those got by the analysis of the soft X-ray discontinuities. Furthermore, fig. 43 on p. 111 of the same paper shows quite clearly the setting in of an enormous increase both of fast electrons which have undergone inelastic impacts and of slow secondary electrons when the primary exciting potential is raised from 47·8 to 69·6 volts. This is just what we should expect if there are two levels, one at least of which is strong, at 53·4 and 63 volts respectively, above the ground level. There is no evidence from Rudberg's velocity analysis of any levels of importance between 27 and 47 volts above the ground level. Judging from Rudberg's curves the low voltage level or levels are weak compared with at least one of the two between 47·8 and 69·6 volts. It should be pointed out that both Rudberg's curves and our analysis of the carbon inflection data were each obtained without any knowledge of, or guidance from, the results of the other.

There is just one final point. It seems that this theory can explain the absence of discontinuities in the soft X-ray or secondary electron excitation curves when polycrystalline metals have not been heated much. The band-like structure is a definite property of a given crystal surface. If the crystals are too small or are strained, crushed and distorted this definiteness should disappear and with it the sharp breaks.

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* 'K. Svensk. Vetensk. Handl.,' vol. 7 (1929).

Summary.

The mechanism of the origin of secondary electrons and of soft X-rays is discussed, particularly in view of the new experimental evidence published by U. Andrewes, Ramachandra Rao, E. Rudberg and the author. The view is put forward that the first act is the excitation of a *structure* electron by the primary which is returned as part of the high energy group of secondaries. The low energy group and the X-rays result from the return of the excited structure electrons to the ground state. The agreement of the soft X-ray with the secondary electron breaks is accounted for, since both are excitation potentials of the structure electrons. The hypothesis gives a natural explanation of the band-like structure of the discontinuities already found empirically for C and Al and here extended to Ni. The soft X-ray data and the analysis of velocity distribution of secondary electrons for carbon have led independently to the same level differences as closely as they have been ascertained. All the levels found are shown to be of the order of magnitude to be expected theoretically.

Homogeneous Catalysis of Gaseous Reactions. Part I.—*The Decomposition of Isopropyl Ether under the Influence of Halides.*

By K. Clusius, Rockefeller Fellow, and C. N. Hinshelwood, F.R.S.

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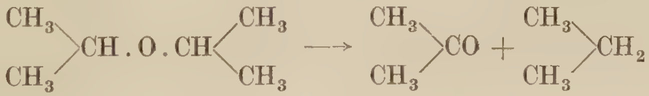
Introduction.

In considering the mechanism of chemical reactions from a general point of view one cannot fail to be impressed by the apparent gulf separating the relatively simple processes occurring in gases from those taking place in solutions. The very common dependence of reactions in solution upon catalytic influences such as those of acid or basic molecules is striking, and does not appear to be nearly so characteristic of gaseous changes. It was recently found* that iodine vapour readily catalysed the gaseous decomposition of isopropyl ether according to the equation :—



$$(CH_3)_2CH.O.CH(CH_3)_2 \longrightarrow (CH_3)_2CO + (CH_3)_2CH_2$$

It seems possible, therefore, that a systematic study of similar reactions may constitute a first step towards bridging the gulf which has been referred to, by revealing under the simpler conditions of the gaseous state the mode of action of a process very commonly observed in solution.

In this first paper the catalytic action of various substances, other than iodine, on the above decomposition will be dealt with. Various alkyl iodides have a considerable catalytic influence, though less than that of iodine. Bromides are much less effective, except hydrogen bromide, the action of which is considerable. Chlorides have practically no influence ; phenyl iodide is also almost inactive. Some typical examples of the various actions are shown in fig. 2.

In the two following papers it is shown that the reaction whereby the hydrogen atom adjacent to the oxygen atom is transferred from one carbon atom to another is a general one, and that under the catalytic influence of iodine the two following changes occur readily :—

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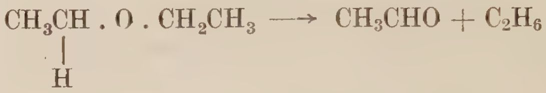
* Glass and Hinshelwood, ' J. Chem. Soc.,' p. 1815 (1929).



$$\mathrm{CH_3\underset{\overset{|}{H}}{C}H\,.\,O\,.\,CH_2CH_3 \longrightarrow CH_3CHO + C_2H_6}$$

$$\mathrm{CH_3CHO \longrightarrow CH_4 + CO}$$

These reactions are homogeneous, and depend upon collisions between molecules of iodine and molecules of the ether or aldehyde. The rates are nearly proportional to the concentration of the catalyst, and the time of half change nearly independent of the ether concentration.

Experimental Method.—The method of measuring the rate of the catalytic decomposition was to observe the pressure change accompanying the reaction, in the manner described in earlier papers. The form of apparatus used was slightly modified, and is represented in fig. 1. A is the silica reaction vessel of about 180 c.c., connected to the rest of the apparatus by a ground joint. From the small bulbs B and C, filled with ether and catalyst respectively, a measured amount of vapour is allowed to stream into A. The pressures are measured on the capillary mercury manometer M, which allows the progress

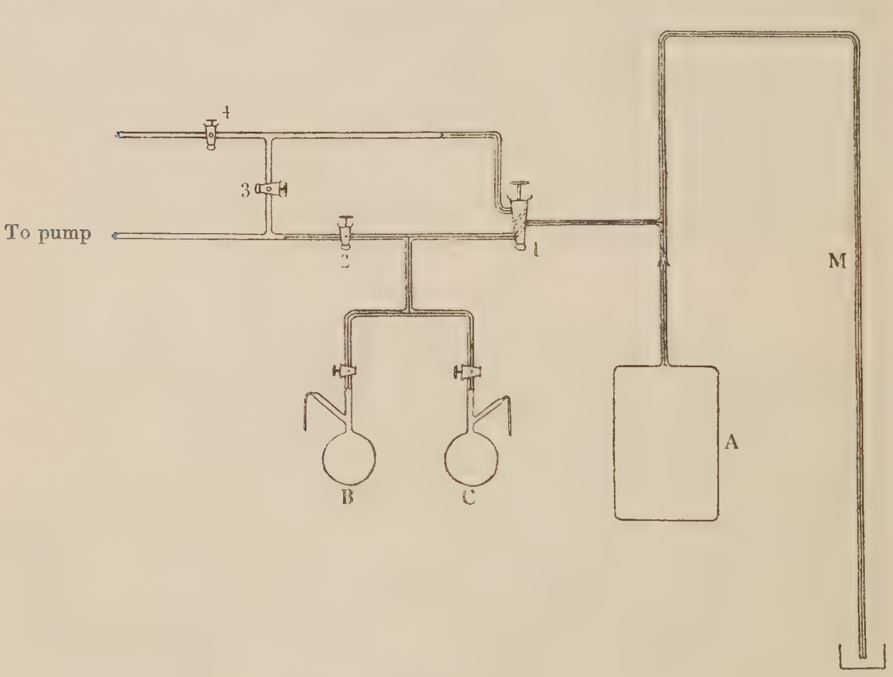


Fig. 1.

of the reaction to be observed. All the capillary tubing is wound with resistance wire and heated electrically to 60–70° C. For this temperature a little sealing wax makes an excellent lubricant of the ground joint. To taps 3 and 4 a gas-holder for taking samples of the reaction products can be attached. The silica vessel was heated by an electric furnace, the temperature of which was measured by a platinum-rhodium thermocouple, and could be kept constant to within 1°.

The results obtained with the different catalysts will be described in order.

Isopropyl Iodide.—It had been observed by Glass and Hinshelwood that undecomposed isopropyl iodide had a certain catalytic action on the decomposition of isopropyl ether. It decomposes itself, however, giving free iodine according to the equation $2C_3H_7I = C_3H_8 + C_3H_6 + I_2$.

When isopropyl iodide is used, the decomposition of the ether accelerates as time goes on. Thus the iodine produced is a better catalyst than the undecomposed iodide. Nevertheless, the initial velocity is great enough to show that the iodide possesses a definite activity of its own.

The following typical experiments, carried out at 332° C., illustrate these facts. In each case the initial pressure of the isopropyl ether was approximately 100 mm.; in the first the catalyst was 23·5 mm. of initially undecomposed isopropyl iodide, and in the second, 24 mm. of the iodide, which was first allowed to decompose, increasing in pressure by 12 mm. in the process.

Time (minutes)	2	4	5	6·5	8	10	12
Per cent. decomposition—							
Undecomposed iodide	7·3	16·2	20·5	26·9	33·1	40·2	46·4
Decomposed iodide	10·9	19·2	22·6	26·4	30·6	35·2	39·5

It will also be noticed that the accelerated decomposition with the undecomposed iodide as catalyst not only overtakes, but actually outstrips the unaccelerated reaction with the decomposed iodide. This, however, is probably a spurious effect due to the fact that the pressure increase caused by the decomposition of the iodide itself is included in the total reaction. The time of half decomposition of 25 mm. isopropyl iodide alone under these conditions was 7·8 minutes. If we compare the initial rates of the two experiments quoted, we find that the 12 mm. iodine present in the one have at least 1½ times the influence of the 23·5 mm. undecomposed iodide in the other.

Ethyl Iodide.—With ethyl iodide as a catalyst an accelerated decomposition of the ether is found (fig. 2). This acceleration is due to the decomposition of the catalyst with liberation of free iodine. At 362° C. the decomposition of the catalyst appears to be complete when about 30 per cent. of the ether has decomposed. Thereafter the decomposition of the ether is in accordance with the unimolecular law and determined solely by the iodine present.

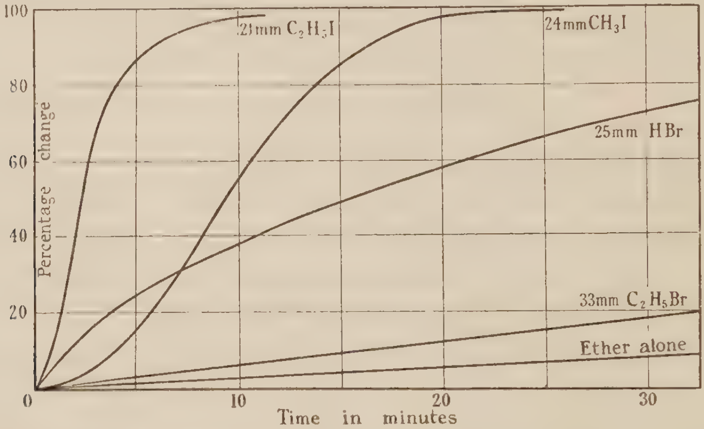


Fig. 2.—Catalysis of the Reaction $C_3H_7 . O . C_3H_7 = C_3H_8 + CH_3 . CO . CH_3$ at 382° C.

The following figures illustrate the accelerated decomposition :—

Temperature 362° C. 100 mm. isopropyl ether. 31 mm. ethyl iodide.

Time (seconds)..	75	115	182	210	258	325	410	501	580
Per cent. change	5·6	11·2	22·5	30·0	40·0	54·0	69·5	81·6	89·4

If these values are plotted from a new origin at 200 seconds, the following table may be obtained :—

t.	x.	$k = \frac{1}{t} \log_{10} \frac{80}{80 - x}$.
seconds	mm. change	
100	22	0·00140
200	40	0·00150
300	53·5	0·00159
400	63	0·00168
∞	80	

The time of half decomposition for this unimolecular part of the reaction is 200 seconds, compared with 305 seconds for the whole reaction. In a number of experiments at different temperatures this ratio of about 2 to 3 was always found.

At 333° C., with 24 mm. ethyl iodide, the half period for the whole decomposition was 1500 seconds. Thus the half period of the "unimolecular" stage of the reaction was 1000 seconds. At the same temperature the time of half decomposition of the ether catalysed by 24 mm. isopropyl iodide, previously decomposed, was 1100 seconds. It is therefore evident that in each case we are dealing simply with catalysis by the iodine.

With ethyl iodide the initial induction is much more marked than with isopropyl iodide, the effect of the undecomposed compound being considerably smaller relative to iodine. From the following figures it is evident that the initial rate with isopropyl iodide is nearly three to four times as great as with ethyl iodide :—

Temperature 333°. 100 mm. isopropyl ether (approx.).

Time (minutes)	2	4	5	6·5
Per cent. change with 20·5 mm. EtI	2·2	4·4	5·4	7·6
Per cent. change with 23 mm. C_3H_7I	7·7	16·2	20·8	27

Methyl Iodide.—Fig. 2 and the following table show that with methyl iodide as a catalyst the induction period is much more marked than with ethyl iodide.

Temperature 361° C. Isopropyl ether 103·5 mm. ; methyl iodide 31 mm.

Time (minutes)	0	2	5·5	7	9	11	13	15
Per cent. changed	0	0	2·4	4·3	7·7	12·5	18·4	24·6
Time (minutes)	17	19	22·5	25	27	28	33	38
Per cent. changed	31·9	41·1	54·5	63·3	71·5	75	89	97·8

The respective values for the times of half change and three-quarter change, t_{50} and t_{75}, are 1270 and 1480 seconds, showing the pronounced acceleration as the change proceeds. Free iodine was found in the products of reaction ; yet experiments made with methyl iodide alone showed it to be stable at this temperature. A mutual decomposition of the isopropyl ether and of the methyl iodide occurs, the free iodine formed having a very much greater catalytic influence than the iodide. This was shown as follows. An amount of methyl iodide equal to that used in the above experiment was left in the reaction vessel for 30 minutes. 101 mm. of the ether were then added. The same induction period as before was found, t_{50} and t_{75} being 1128 and 1510 seconds respectively. Now 100 mm. of methyl iodide with 37 mm. of the ether were let into the reaction vessel. Decomposition occurred, the pressure increasing by 47 mm. The products were withdrawn so as to leave in the vessel an amount of gas equivalent to 31 mm. of the original methyl iodide, and 102·5 mm. of isopropyl ether were added. The reaction was now much more nearly unimolecular; there was no induction period, and the values of t_{50} and t_{75} were 310 seconds and 570 seconds respectively.

From the above table it will be seen that the catalytic action of the undecomposed methyl iodide must be small.

Phenyl Iodide.—The action of phenyl iodide is very small. At 382° C. 11 mm. of phenyl iodide and 116 isopropyl ether gave a change of approximately 18 per cent. in 40 minutes. A blank experiment with the ether gave approximately 11 per cent. in the same time.

As regards the iodides, therefore, it is evident that the catalytic action is inversely proportional to their own stability. The isopropyl ether catalyses their decomposition, and the iodine liberated has a greater influence than any of the undecomposed iodides. From the shape of the curves near the beginning, however, we must conclude that at least isopropyl and ethyl iodides, and probably the other iodides, have a definite action of their own. The activity decreases in the order, isopropyl, ethyl, methyl, phenyl.

Ethyl Bromide.—The action of ethyl bromide is about 50 times smaller than that of ethyl iodide. The reaction accelerates with time: this is due to the gradual decomposition of the ethyl bromide according to the equation

$$C_2H_5Br = C_2H_4 + HBr$$

(no free bromine is produced).

Hydrogen Bromide.—This gas has a considerable action (fig. 2). It is to be noted that there is no induction period or acceleration, the course of the reaction approximating to that of a unimolecular change. Thus at 380° C. with 100 mm. ether, and 25 mm. of hydrogen bromide the values of t_{50} and t_{75} were 930 seconds and 2030 seconds respectively, the ratio required for a unimolecular reaction being 1 : 2.

At 380° C. the half life of the ether with 25 mm. of ethyl iodide as a catalyst is 104 seconds.

It was considered that experiments with hydrogen iodide would be ambiguous owing to its ready decomposition.

Isopropyl bromide and ethylene dibromide gave results analogous to those found with ethyl bromide.

Isopropyl chloride and ethyl chloride had a negligible catalytic action. The hydrogen chloride, produced by their decomposition, is also without catalytic effect.

Analyses.—Some analyses are given to illustrate the fact that the ether decomposes substantially according to the equation

$$C_3H_7 . O . C_3H_7 = CH_3 . CO . CH_3 + C_3H_8.$$

(*a*) 400° C. 172 mm. ether, 16·5 mm. methyl iodide. Total pressure increase = 170 mm.

89·5 mm. products withdrawn, shaken with water, and analysed for acetone by the iodoform method. The acetone found corresponded to 43·1 mm., *i.e.*, 48·2 per cent. The analysis of the gas after removal of acetone vapour gave CO_2, 1·2 per cent.; CO, 5·4 per cent.; C_3H_8, 90·8 per cent.; unsaturated, 2·6 per cent.

The rather high temperature of this experiment tended to favour side decompositions.

(*b*) 380° C. 100 mm. ether, 24·5 mm. hydrogen bromide. Total pressure increase = 98 mm.

Gas washed from acetone vapour gave CO_2, 2·2 per cent.; CO, 3·3 per cent.; unsaturated, 2·1 per cent. The saturated hydrocarbon gave the following results on explosion with oxygen. Gas : Contraction : CO_2 formed = 1 : 2·91 : 2·82 (theoretical for propane, 1 : 3 : 3).

Summary.

The decomposition of isopropyl ether, in the gaseous state,

$$C_3H_7 . O . C_3H_7 = C_3H_8 + CH_3COCH_3,$$

is catalysed not only by iodine, but by various alkyl iodides, and to a smaller extent by alkyl bromides. Chlorides have little influence. Hydrogen bromide is also a good catalyst.

During the decomposition of the ether the alkyl iodides are themselves decomposed, even when they would be stable in the absence of the ether.

The decomposition reaction, whereby a hydrogen atom is transferred under the influence of the catalyst, from one part of the ether molecule to another, with accompanying rupture of the molecule, is a general one.

Homogeneous Catalysis of Gaseous Reactions. Part II.—*The Decomposition of Diethyl Ether Catalysed by Iodine.*

K. Clusius, Rockefeller Fellow, and C. N. Hinshelwood, F.R.S.

(Received April 1, 1930.)

Introduction.

From the analogy of the reaction* $C_3H_7 . O . C_3H_7 = C_3H_8 + (CH_3)_2CO$ it was to be expected that, under the catalytic influence of iodine, diethyl ether would decompose smoothly into ethane and acetaldehyde at a temperature considerably below that at which the normal, and more profound, decomposition becomes appreciable. This anticipation was confirmed by experiment, but it was also found that the acetaldehyde itself suffered a catalytic decomposition into carbon monoxide and methane

$$CH_3 . CH_2 . O . CH_2CH_3 \longrightarrow CH_3 . CH_3 + CH_3CHO \longrightarrow CH_3CH_3 + CH_4 + CO.$$

The kinetics of these reactions are of interest, since Glass and Hinshelwood* found that, in the corresponding catalytic decomposition of isopropyl ether, almost every collision between molecules of iodine and ether in which the kinetic energy of approach exceeded the heat of activation, led to transformation. The energy of activation of the uncatalysed reaction has to be supplied from many " square terms " in the molecules, that of the catalysed reaction from two only. Thus the catalyst by a simple and effective collision brings the energy to the part of the molecule where it is required, in contrast with the wasteful and inefficient collisions between the ether molecules, which result much more rarely in transformation. This view of the matter is further substantiated by the results now to be described.

Experimental Method.—The method of investigation was the same as that described in the preceding paper. The ether was very carefully dried and fractionated, and the iodine was produced in the reaction vessel by the decomposition of pure isopropyl iodide,* $2C_3H_8I = C_3H_8 + C_3H_6 + I_2$. The other products have no influence on the decomposition of ethers.

The rate of reaction is conveniently measurable in the region of 400° C., at which temperature both ether and acetaldehyde are quite stable in the absence of the catalyst.

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* ‘J. Chem. Soc.,’ 1929, p. 1815.

In an experiment at 436° C., 200 mm. of ether were decomposed completely in presence of 17 mm. of the catalyst (*i.e.*, 17/3 mm. of iodine). The products were found to contain :—

Unsaturated hydrocarbon	1·7 per cent.
Carbon monoxide	33·9 ,,
Methane + ethane	64·4 ,,

Combustion of the saturated hydrocarbon gave 1·47 volumes of carbon dioxide for one volume of the gas ; equal proportions of methane and ethane would give 1·50 volumes. Thus the end products correspond to the above equation. A sample of gas withdrawn half-way through the reaction smelt strongly of acetaldehyde and reduced silver solution, showing that the reaction consists of the two consecutive stages. The fact that the actual pressure change on decomposition is a little less than expected is evidently due to some subsidiary condensation reaction. The kinetics are not affected by this, however.

Kinetics of the Reaction.—The velocity of the reaction is expressed by the equations :—

$$-d\,[\text{Ether}]/dt = k_1\,[\text{I}_2]\,[\text{Ether}]$$

$$+d\,[\text{Aldehyde}]/dt = k_1\,[\text{I}_2]\,[\text{Ether}] - k_2\,[\text{I}_2]\,[\text{Aldehyde}].$$

In the following paper it is shown that the aldehyde decomposes approximately 10 times as fast as the ether under comparable conditions. Thus the speed of the whole reaction is principally determined by k_1, and the change follows an approximately unimolecular course, although consisting of consecutive reactions.

The solution to these equations is found as follows. Let a be the initial concentration of ether, expressed in millimetres, and $(a - x)$ the concentration at time t. Let y be the concentration of aldehyde at time t, and z the concentration of carbon monoxide, *i.e.*, the final product. Then, for *unit* concentration of catalyst

$$-\frac{d\,(a-x)}{dt} = k_1\,(a-x),$$

therefore

$$a - x = ae^{-k_1 t}$$

$$\frac{dy}{dt} = k_1\,(a-x) - k_2 y = k_1 a e^{-k_1 t} - k_2 y.$$

Solving the second equation

$$y = \frac{k_1}{k_1 - k_2}\,.\,a\,.\,(e^{-k_2 t} - e^{-k_1 t}).$$

Then

$$\frac{dz}{dt} = k_2 y = \frac{k_1 k_2}{k_1 - k_2} \,.\, a \,.\, (e^{-k_2 t} - e^{-k_1 t})$$

whence

$$z = a \left\{ 1 - \frac{1}{k_1 - k_2} (k_1 e^{-k_2 t} - k_2 e^{-k_1 t}) \right\}.$$

The total pressure increase, by which we measure the progress of the reaction, is $y + 2z$. Let $(y + 2z)/a = \xi$, let $k_1/(k_1 - k_2) = \theta$ and $k_1 t = \tau$, then

$$\xi = \theta \left\{ e^{-\left(1 - \frac{1}{\theta}\right)\tau} - e^{-\tau} \right\} + 2 \left\{ 1 - \theta e^{-\left(1 - \frac{1}{\theta}\right)\tau} - (1 - \theta)\, e^{-\tau} \right\},$$

ξ represents the pressure increase at any time as a fraction of the initial pressure. θ is independent of the amount of catalyst. For a given value of ξ, therefore, in two experiments with different amounts of catalyst, τ must be the same, and therefore t must vary inversely as the amount of catalyst, as it would in a simple unimolecular reaction. In what follows, t_{50} will be taken as the time required for the pressure to attain half its final increase. t_{50} is nearly independent of the initial pressure of ether, and is inversely proportional to the amount of catalyst, as is shown by the following examples.

Temperature.	Initial pressure of ether. a.	Initial pressure of catalyst. c.	t_{50}.	$t_{50} \times c \times 10^{-2}$.
			seconds	
417°	194·5	14·5	1164	169
	173·5	20·5	663	136
	86	24	564	135
443°	184·5	24	186	44·6
	175	22·5	171	38·5
	84	23·5	151	35·5
	175·5	11	357	39·3
464°	186·5	23	106	24·4
	180·5	11	224	24·6
	75·5	24	83	20·0

The above equations contain k_1 and k_2 implicitly, and it would therefore be difficult to extricate the separate values if k_2 could not be determined independently. Experiments with acetaldehyde show, however, that it decomposes about 10 times as fast as ether. Thus to a first approximation we may calculate k_1 by using the equation of a simple unimolecular reaction. A second approximation may be obtained as follows. At 400° C., t_{50} in a given experiment was 955 seconds. Thus to a first approximation $k_1 = (\log_e 2)/955 = 7{\cdot}25 \times 10^{-4}$. An experiment made with acetaldehyde under identical conditions gave $k_2 = 8{\cdot}0 \times 10^{-3}$. Therefore $k_2/k_1 = 80/7{\cdot}25 = 11$. With this ratio of the constants the equation for ξ becomes $\xi = 2 - 2{\cdot}1\, e^{-\tau} + 0{\cdot}1\, e^{-11\tau}$.

ξ may now be plotted as a function of τ, and from the curve the value of τ_{50} corresponding to $\xi = 1$, *i.e.*, to t_{50}, may be read off. The value is $0{\cdot}745$, and since $\tau_{50} = k_1 t_{50}$, $k_1 = 0{\cdot}745/955 = 7{\cdot}8 \times 10^{-4}$. This makes $k_2/k_1 = 10$ approximately. The whole process repeated gives the next approximation for $k_1 = 8{\cdot}0 \times 10^{-4}$, beyond which there is no need to go. It transpires that at any temperature it is accurate enough to find the first approximation, *i.e.*, $k_1 = 0{\cdot}693/t_{50}$, and to increase the result by 10 per cent.

It further appears in the next paper that the decomposition of acetaldehyde has nearly the same temperature coefficient as that of ether. Thus we may take k_2/k_1 as 10 over the whole range of temperature.

We are now in a position to consider the form of the curve connecting time and pressure increase. The following is the result of a typical experiment.

Temperature 443° C. 184·5 mm. diethyl ether, 24 mm. decomposed isopropyl iodide. Total pressure increase on decomposition 334 mm.

Time (seconds), t	42	90	130	165	217	270	334	412	555
Pressure increase x, as percentage of total increase	14·1	27·6	38·0	45·6	56·1	63·5	74·2	83·1	93·3

Since the increase is 334 mm. we take a to be 167 mm.

Now since $k_2/k_1 = 10$, we have $\xi = 2 - 2{\cdot}11\, e^{-\tau} + 0{\cdot}111\, e^{-10\tau}$.

From a curve we can read off the values of τ corresponding to different values of ξ; from a curve of the experimental results we can also read off corresponding values of t, remembering that $\xi = 2$, corresponds to $x = 100$. Corresponding values of ξ and t should be directly proportional to one another. From the experiment quoted we have :—

Per cent. change	10	20	30	40	50	60	70	80
τ	0·15	0·28	0·41	0·57	0·76	0·97	1·27	1·69
t	32	65	100	140	186	242	310	385
$10^2 \times \tau/t$	0·47	0·43	0·41	0·41	0·41	0·40	0·41	0·44

Thus the required proportionality evidently exists.

The following table gives the values of t_{25}, t_{50} and t_{75} at a series of temperatures, showing that the form of the curve does not vary. t_{50} is taken as unity in each case.

	t_{25}.	t_{50}.	t_{75}.
°C			
480·5	0·442	1·00	1·74
462	0·450	1·00	1·78
440·5	0·440	1·00	1·85
415	0·437	1·00	1·83
Average	0·442	1·00	1·80
Theoretical values	0·447	1·00	1·90

Temperature Coefficient.—In determining the temperature coefficient of the reaction velocity it must be remembered that the same pressure of catalyst represents different concentrations at different temperatures. In the following table the values of t_{50} are all reduced so as to correspond to such a concentration of catalyst as would produce a pressure of 20 mm. (*i.e.*, 6·7 mm. iodine) at 700° absolute.

Temperature (absolute).	t_{50}. (average value).	t_{50}. (calculated).
°	seconds	seconds
766	42	38
740	81·5	87
721	166	166
701	339	339
681	736	697

The value of t_{50}, calculated, are obtained from the equation

$$-d \log_e t_{50}/dT = E/RT^2,$$

taking the value of E as 35,000 calories.

Since k_1 governs the rate of reaction principally, and moreover since, as appears in the following paper, k_2 has nearly the same temperature coefficient, this value may be regarded as the heat of activation corresponding to k_1, *i.e.*, to the initial decomposition of the ether.

Molecular Statistics of the Reaction.—Experiments made in a bulb packed with beads of silica showed that the surface reaction could not amount to more than a few per cent. of the total. Thus reaction must depend upon collisions between molecules of ether and molecules of iodine. The number of collisions between unlike molecules is given by the expression

$$Z = N_1 N_2 \sigma_{12}^2 \left\{ 8\pi RT \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \right\}^{\frac{1}{2}}.$$

N_1 and N_2 are the numbers of molecules of the two kinds per cubic centimetre ; σ_{12} is the mean of the molecular diameters ; m_1 and m_2 are the respective molecular weights. We will take as the standard condition 400° C., 760 mm. ether, and a concentration of iodine which gives a pressure of 6·7 mm. at 700° absolute. Then $N_1 = 1{\cdot}10 \times 10^{19}$; $N_2 = 0{\cdot}92 \times 10^{17}$; $m_1 = 74$, $m_2 = 254$. σ_{12} is taken as $\frac{1}{2}(5 + 3{\cdot}76) \times 10^{-8}$ cm. $= 4{\cdot}38 \times 10^{-8}$ cm. From this $Z = 3{\cdot}02 \times 10^{26}$.

At 400° C., $k_1 = 8{\cdot}0 \times 10^{-4}$. Therefore the number of molecules reacting per second per cubic centimetre at 760 mm. is

$$k_1 N_1 = 8{\cdot}0 \times 10^{-4} \times 1{\cdot}10 \times 10^{19} = 8{\cdot}8 \times 10^{15}.$$

E is 35,000 calories ; corrected for the variation in the collision number with temperature* by subtracting $\frac{1}{2}RT$, this becomes 34,300 calories.
Then

$$Ze^{-E/RT} = 3{\cdot}02 \times 10^{26} \times e^{-34{\cdot}300/1{\cdot}98 \times 673} = 2{\cdot}1 \times 10^{15}.$$

Thus within a factor of four times the number of molecules reacting is equal to the number which collide having a kinetic energy of approach (or in general a total energy in two square terms) greater than E. Whether the discrepancy has a real significance or not cannot be decided.† The important fact is that a very simple assumption about a collision mechanism leads to a result which is of the right order of magnitude.

The course of the uncatalysed reaction is usually less simple ; and therefore it is of interest to note that the catalytic reaction has in all cases a considerably smaller activation energy.

Decomposition of	$C_3H_7 . O . C_3H_7$	$C_2H_5 . O . C_2H_5$	CH_3CHO
$E_{\text{uncatalysed}}$	60,500	53,500	45,500
$E_{\text{catalysed}}$	28,500	34,300	32,500

In the one case there is a general break up of the molecule caused by collision between two ether molecules, for example, with a large amount of energy. In the other case the catalyst brings a smaller amount of energy to a point in the molecule where it is more effectively and economically utilised.

Summary.—The catalytic decomposition of diethyl ether under the influence of iodine occurs by two consecutive reactions :—

$$CH_3CH_2 . O . CH_2CH_3 \longrightarrow CH_3 . CH_3 + CH_3CHO \longrightarrow CH_3CH_3 + CH_4 + CO\cdot$$

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* "Kinetics of Chemical Change," p. 104 (Oxford, 1929).

† *Ibid.*, p. 100.

The kinetic equations of unimolecular consecutive reactions are obeyed, the velocity constants being proportional to the iodine concentration. The constant for the second reaction is 10 times greater than that for the first.

Every collision between ether and iodine in which the kinetic energy of approach exceeds 34,300 calories probably leads to decomposition.

The heats of activation of this and similar reactions are lower than those of the corresponding uncatalysed reactions, and the mechanism of activation simpler. The catalyst seems to attack a complex molecule at one specific point.

Homogeneous Catalysis of Gaseous Reactions. Part III.—*The Decomposition of Acetaldehyde Catalysed by Iodine.*

C. N. Hinshelwood, F.R.S., K. Clusius, Rockefeller Fellow, and G. Hadman, Scholar of St. John's College, Oxford.

(Received April 1, 1930.)

The normal decomposition of acetaldehyde into carbon monoxide and methane is bimolecular, and occurs with conveniently measurable velocity at 500° C. and above. At 400° C. the rate is very small indeed. In presence of small amounts of iodine a rapid catalytic reaction takes place.

This reaction was investigated by the method described in the preceding papers. As before, the iodine was produced by the decomposition of isopropyl iodide in the reaction vessel. The supply of liquid acetaldehyde, from which vapour was drawn off for the experiments, had been freshly distilled in an all-glass apparatus, and boiled between 21° and 22° C.

The increase in pressure attending the decomposition was never quite equal to that theoretically demanded by the equation $CH_3CHO = CH_4 + CO$, a small proportion of the aldehyde apparently being lost in a simultaneous condensation reaction. For example, 299 mm. acetaldehyde gave an increase of 275 mm. The products contained 49·8 per cent. carbon monoxide, 48·5 per cent. methane, and 1·7 per cent. unsaturated hydrocarbon. Since the latter came from the catalyst, it appears that the reaction is a simple decomposition into carbon monoxide and methane. The small amount of condensation reaction does not appear to affect the kinetics in any way.

The reaction is unimolecular with respect to the aldehyde, and its rate is directly proportional to the concentration of the catalyst.

$$-d\,[CH_3CHO]/dt = k\,[CH_3CHO]\,[I_2].$$

Since $[I_2]$ does not change in the course of a given experiment we have the simple formula $k = \frac{1}{t} \log \frac{a}{a - x}$, a and x being the initial amount of aldehyde and the amount transformed at time t respectively.

The following two typical experiments show that with a constant concentration of catalyst the reaction is unimolecular.

Temperature 420°. Catalyst 13 mm.

Initial pressure of aldehyde 239 mm.			Initial pressure of aldehyde 120 mm.		
t.	x.	k_{10} (decimal logarithms).	t.	x.	k_{10}.
seconds			seconds		
7	20	0·0061	8	10	0·00564
15	40	0·0060	17	20	0·00555
32	75	0·0059	27	30	0·00553
42	90	0·0057	38	40	0·00560
56	110	0·0056	50	50	0·00575
81	140	0·0057	64	60	0·00589
102	160	0·0059	81	70	0·00605
132	180	0·0061	∞	103·5	
∞	213				
	Average	0·00588		Average	0·00572

The influence of the concentration of catalyst is shown below.

Temperature 391° C.

Catalyst.	k_{10}.	k_{10}/Catalyst × 10^4.
(mm.)		
10	0·00193	1·93
20	0·00377	1·89
30	0·00559	1·86

These results establish the validity of the equation given above.

To determine the temperature coefficient of the reaction velocity, experiments were made at five temperatures, using 20 mm. of catalyst (decomposed isopropyl iodide) in each case. The results were reduced to a standard concentration of catalyst, namely, that corresponding to a pressure of 20 mm. at 700° absolute, by using the linear relation between velocity constant and amount of catalyst. In the following table, t_{50} is the time in seconds required for half the aldehyde to decompose, and is connected with the true velocity constant, k, by the relation $t_{50} = \frac{1}{k} \log_e 2$.

Temperature (absolute).	t_{50} (seconds).		Average t_{50} (corrected).	$k \times 10^4$.	$k \times 10^4$ (calculated).
° 695·5	30 33·8 30·5	average 31·4	31·6	220	219
676	56·5 57	,, 56·8	58·6	118	112
663	93 99	,, 96	101	68·6	67·6
647	191 174	,, 182	197	35·2	35·5
631	342 325	,, 333	369	18·8	18·6

From the formula $d \log k/d\text{T} = \text{E}/\text{RT}^2$ the value of E is found to be 33,200 calories. The calculated values of k in the last column are obtained from this. When corrected for the variation in the collision number with temperature, E becomes 32,500 calories.

As before, we will now calculate the relation between the number of molecules reacting and the number entering into collision with molecules of the catalyst. At 400° C., k is $9 \cdot 8 \times 10^{-3}$ when the concentration of the decomposed isopropyl iodide is such as to correspond to 20 mm. at 700° absolute (*i.e.*, the iodine pressure is 20/3 mm.). The number of molecules of aldehyde per cubic centimetre at 400° C. and 760 mm. is $1 \cdot 10 \times 10^{19}$. Therefore the number reacting per cubic centimetre per second at this pressure is

$$1 \cdot 10 \times 10^{19} \times 9 \cdot 8 \times 10^{-3} = 10 \cdot 8 \times 10^{16}.$$

The number of collisions between aldehyde and iodine is calculated, as before, from the formula

$$Z = N_1N_2\sigma_{12}^2\left\{8\pi RT\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\right\}^{\frac{1}{2}}$$

$$N_1 = 1\cdot10\times10^{19},\quad N_2 = 0\cdot92 = 10^{17},\quad \sigma_{12} = 4\cdot38\times10^{-8}\ \text{cm.}$$

$$m_1 = 44,\quad m_2 = 254,\quad R = 1\cdot98\times4\cdot18\times10^7\ \text{ergs per degree.}$$

Whence $Z = 3\cdot74\times10^{26}$.

If we assume that each collision between aldehyde and iodine is effective when the kinetic energy of approach exceeds the energy of activation, we obtain for the number of molecules which should react,

$$Ze^{-E/RT} = 3\cdot74\times10^{26}\times e^{-32{,}500/1\cdot98\times673} = 9\cdot7\times10^{15}.$$

This is 10 times smaller than the number actually reacting, as compared with four times smaller in the corresponding calculation for diethyl ether, and equality for di-isopropyl ether. While it may well be that the discrepancy is due to a certain small error in E, and to the assumption of too small a diameter for the aldehyde molecule, it is also quite possible that the internal energy of the molecules is drawn upon to provide some of the energy of activation. If we introduce one internal degree of freedom in addition to the translational energy, we obtain for the number which might react

$$Ze^{-(E+RT)/RT}\left(\frac{E+RT}{RT}\right).$$

(See Hinshelwood, 'Kinetics of Chemical Change in Gaseous Systems,' 2nd ed., p. 102.) The numerical value of this is $9\cdot4\times10^{16}$ in almost exact agreement with the number observed. Another possibility is that the number of collisions is really somewhat greater than calculated, on account of the greater speeds of the molecules which participate in an activating collision. But in any case the important fact is again that the absolute speed can be calculated as regards order of magnitude by assuming a quite simple mechanism of activation.

Summary.

The catalytic decomposition* of acetaldehyde in presence of iodine takes place in accordance with the equation

$$-\frac{d\,[CH_3CHO]}{dt} = k\,[CH_3CHO]\,[I_2].$$

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* Collisions between hydrogen and acetaldehyde molecules cause decomposition at higher temperatures ('Roy. Soc. Proc.,' A, vol. 116, p. 163 (1927)).

This is a convenient place to record some experiments, carried out by Askey and Hinshelwood, which showed that pure nitrogen, from sodium azide, also accelerates the

The heat of activation, corrected for variation of the collision number with temperature is 32,500 calories.

The assumption that the energy of activation is supplied by the collisions between aldehyde and iodine molecules leads to a calculated rate of reaction 10 times smaller than the observed. The assumption that the energy is also derived from one internal degree of freedom brings the calculated and observed rates into agreement.

New Results of the Magnetic Spectroscopy of X-Ray Electrons.

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§ 1. *Introductory.*

In these experiments, pencils of the secondary, ... tertiary, cathode rays, emitted from the surface of a selected "target" which is bombarded by X-rays, are separated by an approximately homogeneous magnetic field ; they are then, by means of a well-known focussing device, photographed as a sort of magnetic spectrum. Sufficiently detailed descriptions of the method are given in previous papers, which will be referred to as I to IV respectively.*

The primary radiation used in most of the new work was silver K + "white"

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decomposition of aldehyde slightly. The experiments were made at 518° C., and the results were :—

Initial pressure of aldehyde (mm.)	192	190	190	190
Initial pressure of nitrogen (mm.)	0	401	700	992
Time of half decomposition	12′ 25″	10′ 25″	9′ 7″	8′ 5″

From the various investigations, we may compare the influence of the different gases on the decomposition. If we write

$$-d[CH_3CHO]/dt = k[CH_3CHO]^2 + k_H[H_2][CH_3CHO] + k_N[N_2][CH_3CHO] + k_I[I_2][CH_3CHO]$$

then at 518° C., $k = 8{\cdot}4 \times 10^{-6}$, $k_H = 7{\cdot}4 \times 10^{-7}$, $k_N = 5 \times 10^{-7}$, while k_I (by extrapolation) $= 5{\cdot}2 \times 10^{-2}$. The unit of concentration is the millimetre at 518°.

* (I) Robinson and Rawlinson, 'Phil. Mag.,' vol. 28, p. 277 (1914) ; (II) Robinson, 'Roy. Soc. Proc.,' A, vol. 104, p. 455 (1923) ; (III) Robinson, 'Phil. Mag.,' vol. 50, p. 241 (1925) ; (IV) Robinson and Cassie, 'Roy. Soc. Proc.,' A, vol. 113, p. 282 (1926).

radiation—practically unfiltered radiation from a gas-filled tube with silver anticathode. The results obtained in this part of the work are tabulated below in § 2. Kellström's* values have been taken for the characteristic lines in the primary beam :—

Line.	ν/R.
Ag $K\alpha_1$	1632·3
$K\alpha_2$	1619·6
$K\beta_3$	1834·8
$K\beta_1$	1837·2
$K\beta_2$	1875·0

The same values as before are taken for the fundamental constants required in translating magnetic deflections of electrons into the equivalent values of ν/R, for comparison with X-ray spectroscopic data ($e/m_0 = 1{\cdot}7686 \times 10^7$ E.M.U./gm. ; $e = 4{\cdot}774 \times 10^{-10}$ E.S.U. ; $h = 6{\cdot}545 \times 10^{-27}$ erg sec. ; $c = 3 \times 10^{10}$ cm./sec. ; $R = 109737$). These are possibly no longer the best available values, but in view of the complicated way in which the constants enter into the calculations, and of the prevailing uncertainty as to their probable accuracy,† it has not been considered expedient at this stage to re-compute our existing conversion tables. It may, however, be mentioned that new work with softer primary radiations (now in progress in this laboratory) has confirmed the sign and approximate magnitude of discrepancies already noted (*e.g.*, IV, p. 294) between our results and those taken from the spectroscopic tables. It is possible that further work here may furnish evidence which can materially assist in the revision of the fundamental constants.

The *level values* and *emission lines* quoted in § 2 have been taken respectively from Coster's table in Müller-Pouillet and from the summaries given by Lindh,‡ except where more recent values are available. There is still some doubt as to the accuracy of the X-ray terms, especially with those of lower frequency.§

Intensities (column 2 of § 2) are visual estimates on an arbitrary scale 1–6, 6 corresponding to the strongest lines. Column 3 gives rH in gauss centimetres, column 4 the equivalent ν/R, and column 5 (" origin ") as far as possible the level from which the electron has been expelled. This is generally quite clear in the case of secondary cathode ray groups, *i.e.*, of electrons expelled from atoms of the target by the direct action of the monochromatic radiations in the primary beam. It is less clear in other cases, where the photoelectron receives its energy during an internal rearrangement within the atom, while the atom is passing to an excited state of lower energy. These " photoelectrons of the second kind " are indicated by the letter " F " in column 5. For the sake of brevity, the corresponding lines of the corpuscular spectra are spoken of as " fluorescent lines," and in the tables they are treated as though they are due to the internal absorption of the fluorescent X-ray spectrum excited in the target (*cf.* IV, p. 298). The assumed level of origin is accented to indicate the fact that it is a level, not in the normal X-ray scheme, but in an atom which is left doubly ionised. The appropriate emission lines of the target are given at the head of each table, with their systematic descriptions ($M_V - L_{III}$, etc.), for convenience of reference. We use the dash (—) in $M_V - L_{III}$, etc., as symbolic of the " electron jump," and it will be understood that, for example, " Origin : F : $L\alpha_1 - M_{III}'$ " may be taken simply as a convenient abbreviation for the process : transition $M_V - L_{III}$* + expulsion of an M_{III} electron, or symbolically, $M_V \rightarrow L_{III} : M_{III} \rightarrow \infty$. In general there are obvious alternative processes which give similar values for the balance of energy carried off by the photoelectron† ; as a rule we give only the most obvious combination, which suffices to classify the line. The fluorescent lines will be dealt with at greater length in § 5.

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* Kellström, 'Z. Physik,' vol. 41, p. 516 (1927).

† *Cf.* Birge, 'Phys. Rev.,' Supplement, vol. 1, p. 1 (1929). The latest experimental value for e is $4{\cdot}821 \times 10^{-10}$ E.S.U. (Cork, 'Phys. Rev.,' vol. 35, p. 128 (1930)).

‡ 'Physik. Z.,' vol. 28, pp. 24, 93 (1927).

§ *Cf.* Johnson, 'Phys. Rev.,' vol. 34, p. 1106 (1929).

It may be advisable to repeat here, before proceeding to the tables, that our " lines " are in fact broad bands, sharply defined only on their high-velocity edges. If, therefore, two lines are not sufficiently separated, only the one of higher energy can be accurately measured, and there is always an element of doubt as to the relative intensity of its companion. Where the separation is excessively small, the line of lower energy entirely escapes observation, unless it is relatively very intense. This explains the absence from the tables of a number of lines which would otherwise have been recorded.

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* *i.e., transition of the atom* from the L_{III} to the M_V state.

† For example, $\nu/R\ (Ll - M_V)$ clearly $= \nu/R\ (L\alpha_1 - M_I)$.

§ 2. *Table of Results.*

92. URANIUM (Oxide).

Level Values :	L_{I} 1603·5	M_{I} 408·9	N_{I} 106·6	O 23·9–6·0
	L_{II} 1543·1	M_{II} 382·1	N_{II} 95·7	P 2·7–1·8
	L_{III} 1264·3	M_{III} 317·2	N_{III} 77·1	
		M_{IV} 274·0	N_{IV} 56·3	
		M_{V} 261·0	N_{V} 53·6	
			N_{VI} 28·4	
			N_{VII} 27·6	

Emission Lines : $L\alpha_1$ (M_{V} — L_{III}) 1003·2; $L\beta_1$ (M_{IV} — L_{II}) 1269·1;
$L\beta_2$ (N_{V} — L_{III}) 1210·7; $L\beta_3$ (M_{III} — L_{I}) 1286·2;
$L\gamma_1$ (N_{IV} — L_{II}) 1487·0; Ll (M_{I} — L_{III}) 855·8.

Remarks.	Intensity.	*r*H.	ν/R.	Origin.
	2	301·0	587·1	F : $L\alpha_1$ — 416·1 (M_{I}')
	3	310·0	622·5	F : $L\alpha_1$ — 380·7 (M_{II}')
	2	313·9	638·1	
	2	321·0	667·0	
	3	324·4	681·1	F : $L\alpha_1$ — 322·1 (M_{III}')
	3–4	334·0	721·7	F : $L\alpha_1$ — 281·5 (M_{IV}')
	3	335·9	729·8	F : $L\alpha_1$ — 273·4 (M_{V}')
	2	339·3	744·5	F : Ll — 111·3 (N′)
	2	360·0	837·3	F : Ll — 18·5 (O′)
	2–3	371·5	890·8	F : $L\alpha_1$ — 112·4 (N′); $L\beta_1$ — 378·3 (M_{II}' ?); $L\beta_2$ — 319·9 (M_{III}')
Not completely resolved	3	379·8	930·6	F : $L\alpha_1$ — 72·6 (N′); $L\beta_2$ — 280·1 (M_{IV}')
	4–5	382·6	944·1	F : $L\alpha_1$ — 59·1 (N′); $L\beta_1$ — 325·0 (M_{III}'); $L\beta_2$ — 266·6 (M_{V}')
	2	389·0	975·6	F : $L\alpha_1$ — 27·6 (N′)
	3	394·0	1000·5	F : $L\alpha_1$ — 2·7 (O′, P′); $L\beta_1$ — 268·6 (M_{V}')
Doubtful line	1–2	406·0	1061·5	
Doubtful line	1	414·8	1107·4	
Doubtful line	0–1	419·5	1132·2	
Doubtful line	0–1	427·5	1175·2	
Not completely resolved	3	433·6	1208·5	M_{I} : Ag $K\alpha_2$ — 411·1
	4+	436·4	1223·8	M_{I} : Ag $K\alpha_1$ — 408·5
	3—	438·9	1237·7	M_{II} : Ag $K\alpha_2$ — 381·9
	4	441·3	1251·0	M_{II} : Ag $K\alpha_1$ — 381·3
Not completely resolved	4	450·1	1300·6	M_{III} : Ag $K\alpha_2$ — 319·0
	6	452·7	1315·4	M_{III} : Ag $K\alpha_1$ — 316·9
Not completely resolved	4+	457·8	1344·8	M_{IV} : Ag $K\alpha_2$ — 274·8
Not completely resolved	4+	459·9	1356·8	M_{IV}, M_{V} : Ag $K\alpha_1$ — 275·5; Ag $K\alpha_2$ — 262·8
	4	462·4	1371·4	M_{V} : Ag $K\alpha_1$ — 260·9
Head of a narrow band ?	2–3	472·5	1430·8	M_{I} : Ag $K\beta_1$ — 406·4
	3	476·9	1457·1	M_{II} : Ag $K\beta_1$ — 380·1
	2	481·5	1484·8	F : $L\gamma_1$ — 2·2 (O′, P′)
	3+	487·7	1522·5	M_{III} : Ag $K\beta_1$ — 314·7; N_{I} : Ag $K\alpha_1$ — 109·8
	2+	491·1	1543·4	$N_{II, III}$: Ag $K\alpha_1$ — 88·9

92. URANIUM (Oxide)—(continued).

Remarks.	Intensity.	*r*H.	ν/R.	Origin.
Head of a narrow band	3	493·5	1558·3	Ag $\mathrm{K\beta_1 - M_{IV}}$; $\mathrm{K\beta_2 - M_{III}}$; $\mathrm{K\alpha - N}$.
	2	496·4	1576·2	Ag $\mathrm{K\beta_1 - M_{V}}$; $\mathrm{K\alpha_1 - N_{IV,\,V}}$.
Not completely resolved	3	502·7	1615·7	O : Ag $\mathrm{K\alpha_1}$ − 16·6
	2	503·6	1621·4	O : Ag $\mathrm{K\alpha_1}$ − 10·9
Diffuse band, with complex structure	2	509·0	1655·5	
	1	510·8	1667·1	
	1−	512·6	1678·6	
	1+	520·0	1726·3	$\mathrm{N_I}$: Ag $\mathrm{K\beta_1}$ − 110·9
	1	524·5	1755·7	$\mathrm{N_{II,\,III}}$: Ag $\mathrm{K\beta_1}$ − 81·5
	0–1	534·7	1823·0	N, O : Ag $\mathrm{K\beta_1}$ − 14·2 ; $\mathrm{K\beta_2}$ −54·0
	1+	544·7	1890·2	(?)

Note.—Ag Kα — UM, N region also contains ULβ and Lγ fluorescent lines.

83. BISMUTH (Oxide).

Level Values :

$\mathrm{L_I}$	1207·9	$\mathrm{M_I}$	295·9	$\mathrm{N_I}$	71·0	O	11·2–2·0
$\mathrm{L_{II}}$	1159·4	$\mathrm{M_{II}}$	273·6	$\mathrm{N_{II}}$	58·7	P	0·1
$\mathrm{L_{III}}$	990·0	$\mathrm{M_{III}}$	234·0	$\mathrm{N_{III}}$	50·3		
		$\mathrm{M_{IV}}$	199·4	$\mathrm{N_{IV}}$	35·7		
		$\mathrm{M_{V}}$	191·4	$\mathrm{N_{V}}$	33·7		
				$\mathrm{N_{VI}}$	13·6		
				$\mathrm{N_{VII}}$	13·0		

Emission Lines : $\mathrm{L\alpha_1}$ ($\mathrm{M_V - L_{III}}$) 798·5 ; $\mathrm{L\beta_1}$ ($\mathrm{M_{IV} - L_{II}}$) 959·9 ; $\mathrm{L\beta_2}$ ($\mathrm{N_V - L_{III}}$) 956·3 ; $\mathrm{L\gamma_1}$ ($\mathrm{N_{IV} - L_{II}}$) 1124·1 ; Ll ($\mathrm{M_I - L_{III}}$) 694·1 ; $\mathrm{L\gamma_6}$ ($\mathrm{O_{IV} - L_{II}}$) and $\mathrm{L\gamma_3}$ ($\mathrm{N_{III} - L_I}$) 1157·5 ; $\mathrm{L\gamma_4}$ ($\mathrm{O_{II,\,III} - L_I}$) 1196·8.

Remarks.	Intensity.	*r*H.	ν/R.	Origin.
	3+	271·5	478·3	$\mathrm{L_{II}}$: Ag $\mathrm{K\alpha_1}$ − 1154·0
	2	278·6	503·4	F : $\mathrm{L\alpha_1}$ − 295·1 ($\mathrm{M_I'}$)
	2	282·9	519·1	F : $\mathrm{L\alpha_1}$ − 279·4 ($\mathrm{M_{II}'}$)
	2	288·3	539·0	
	3	294·1	560·7	F : $\mathrm{L\alpha_1}$ − 237·8 ($\mathrm{M_{III}'}$)
	4	303·4	596·4	F : $\mathrm{L\alpha_1}$ − 202·1 ($\mathrm{M_{IV}'}$)
	1–2	305·6	605·1	F : $\mathrm{L\alpha_1}$ − 193·4 ($\mathrm{M_{V}'}$)
Not completely resolved (*a*)	3–4	312·8	633·7	$\mathrm{L_{III}}$: Ag $\mathrm{K\alpha_2}$ − 985·9
	5	316·0	646·6	$\mathrm{L_{III}}$: Ag $\mathrm{K\alpha_1}$ − 985·6 ; F : Ll − N′
	2–3	325·3	684·8	$\mathrm{L_{II}}$: Ag $\mathrm{K\beta_1}$ − 1151·4 ; F : $\mathrm{L\beta_1}$ − 275·1 ($\mathrm{M_{II}'}$)
	2–3	334·1	722·1	F : $\mathrm{L\alpha_1}$ − 76·4 (N′) ; $\mathrm{L\beta_1}$ − 237·8 ($\mathrm{M_{III}'}$) ; $\mathrm{L\beta_2}$ − 234·2

(*a*) Ag Kβ_1 — Bi$\mathrm{L_I}$ also here.

83. BISMUTH (Oxide)—(continued).

Remarks.	Intensity.	rH.	ν/R.	Origin.
	5	344·2	765·9	F : Lα_1 — 32·6 (N′); Lβ_1 — 194·0 ($\mathrm{M_{IV,V}}'$)
	2	349·9	791·2	F : Lα_1 — 7·3 (O′, P′)
	1–2	356·8	822·4	F : Lγ_1 — 301·7 ($\mathrm{M_I}'$)
	3	363·3	852·4	$\mathrm{L_{III}}$: Ag Kβ_1 — 984·8; F : Lγ_1 — 271·7 ($\mathrm{M_{II}}'$)
	2	370·3	885·1	F : Lγ_1 — 239·0 ($\mathrm{M_{III}}'$); Lβ_1 — 74·8 (N′)
	3+	379·3	928·1	F : Lγ_1 — 196·0 ($\mathrm{M_{IV,V}}'$); Lβ_1 — 31·8 (N′)
	1–2	385·6	958·8	F : Lβ_1 — 1·1 (O′, P′); L$\gamma_{6,3}$ — $\mathrm{M_V}'$
	0–1	394·9	1005·0	F : Lγ_4 — 191·8 ($\mathrm{M_V}'$)
	0·1	431·5	1196·9	F : Lγ_4 — O′
Not completely resolved	1	453·5	1320·0	
Not completely resolved	3	455·2	1329·7	$\mathrm{M_I}$: Ag Kα_2 — 289·9
	4+	457·2	1341·3	$\mathrm{M_I}$: Ag Kα_1 — 291·0
	4—	461·2	1364·4	$\mathrm{M_{II}}$: Ag Kα_1 — 267·9
Not completely resolved	3+	465·5	1389·5	$\mathrm{M_{III}}$: Ag Kα_2 — 230·1
	5–6	467·8	1403·0	$\mathrm{M_{III}}$: Ag Kα_1 — 229·3
Narrow band	4–5	474·9	1445·1	$\mathrm{M_{IV}}$, $\mathrm{M_V}$: Ag Kα_1 — 187·2
	1–2	480·4	1478·2	
	1–2	484·8	1504·8	
	2	491·3	1544·6	$\mathrm{M_I}$: Ag Kβ_1 — 292·6
	4	495·1	1568·2	$\mathrm{M_{II}}$: Ag Kβ_1 — 269·0; N : Ag Kα_1 — 64·1
	2	498·0	1586·2	N : Ag Kα_1 — 46·1
	3	501·0	1605·1	$\mathrm{M_{III}}$: Ag Kβ_1 — 232·1; N : Ag Kα_1 — 27·2
	1–2	508·4	1651·8	$\mathrm{M_{IV,V}}$: Ag Kβ_1 — 185·4
Not completely resolved	2	526·1	1766·2	N : Ag Kβ_1 — 71·0
	1	527·5	1775·3	N : Ag Kβ_1 — 61·9
Doubtful line	1	528·9	1784·5	N : Ag Kβ_1 — 52·7
	1	536·5	1835·0	O : Ag Kβ_1 — 2·0
	1	545·8	1897·6	(?)
	0–1	553·7	1951·6	(?)

82. LEAD (Element).

Level Values :				
L_{I} 1169·3	M_{I} 283·8	N_{I} 66·0	O 10·3–0·8
L_{II} 1121·9	M_{II} 262·3	N_{II} 55·4	
L_{III} 960·5	M_{III} 226·0	N_{III} 49·3	
	M_{IV} 190·5	N_{IV} 32·2	
	M_{V} 183·0	N_{V} 30·5	
		N_{VI} 10·8	
		N_{VII} 10·3	

Emission Lines : $L\alpha_1$ $(M_{V} - L_{III})$ 777·5; $L\beta_1$ $(M_{IV} - L_{II})$ 930·0; $L\beta_2$ $(N_{V} - L_{III})$ 930·0; $L\gamma_1$ $(N_{IV} - L_{II})$ 1088·4; $L\beta_3$ $(M_{III} - L_{I})$ 943·3; Ll $(M_{I} - L_{III})$ 676·7.

Remarks.	Intensity.	*r*H.	*ν*/R.	Origin.
Doubtful line; one plate only	2	242·4	381·8	
Doubtful line; one plate only	3	280·8	509·1	L_{II} : Ag $K\alpha_1$ — 1123·2; F : $L\alpha_1$ — 268·4 (M_{II}')
	4	289·7	544·2	F : $L\alpha_1$ — 233·3 (M_{III}')
Not completely resolved	5	300·4	584·8	F : $L\alpha_1$ — 192·7 (M_{IV}')
	3	301·9	590·6	F : $L\alpha_1$ — 186·9 (M_{V}')
	2	310·0	622·5	F : Ll — 54·2 (N')
Not completely resolved (*a*)	4	319·0	658·8	L_{III} : Ag $K\alpha_2$ — 960·8
Head of a narrow band (*a*)	5–6	322·2	672·0	L_{III} : Ag $K\alpha_1$ — 960·3
Doubtful line	0–1	323·3	676·6	F : Ll — O'
Narrow band	3	329·3	701·6	F : $L\beta_1$ — 228·4 (M_{III}')
	2	333·3	718·7	L_{II} : Ag $K\beta_1$ — 1118·5; F : $L\alpha_1$ — 58·8 (N')
	5–6	338·8	742·3	F : $L\alpha_1$ — 35·2 (N'); $L\beta_1$ — 187·7 $(M_{IV,V}')$
Doubtful line	1	339·2	744·1	F : $L\alpha_1$ — 33·4 (N'); $L\beta_1$ — 185·9 (M_{V}')
	3	345·7	772·6	F : $L\alpha_1$ — 4·9 (O')
Narrow band	3	368·6	877·1	L_{III} : Ag $K\beta_1$ — 960·1; F : $L\beta_1$ — N'; $L\gamma_1$ — M_{III}'
	2–3	372·8	897·0	F : $L\gamma_1$ — 191·4 $(M_{IV,V}')$; $L\beta_{1,2}$ — N'
Doubtful line	1	384·4	952·9	
Doubtful line	0–1	397·5	1018·1	
Doubtful line	0–1	439·0	1238·2	
Broad	4+	458·9	1351·1	M_{I} : Ag $K\alpha_1$ — 281·2
Sharp	4	462·0	1369·1	M_{II} : Ag $K\alpha_1$ — 263·2
Not completely resolved	4–5	465·9	1391·8	M_{III} : Ag $K\alpha_2$ — 227·8
	6	468·0	1404·2	M_{III} : Ag $K\alpha_1$ — 228·1
Broad band	4+	475·1	1446·3	$M_{IV,V}$: Ag $K\alpha_1$ — 186·0
	2	481·6	1485·4	
	2	486·9	1517·6	
Not completely resolved	4–5	492·6	1552·6	M_{I} : Ag $K\beta_1$ — 284·6; N : Ag $K\alpha_2$ — 67·0
Head of a narrow band	4	496·7	1578·1	M_{II} : Ag $K\beta_1$ — 259·1; N : Ag $K\alpha_1$ — 54·2
Head of a narrow band	3	503·6	1621·4	N : Ag $K\alpha_1$ — 10·9; Ag $K\beta_1$ — M_{III} unresolved
	1–2	508·1	1649·9	$M_{IV,V}$: Ag $K\beta_1$ — 187·3
	2	512·5	1677·9	
	1–2	520·3	1728·2	
Narrow band; complex structure	2	527·6	1776·0	N : Ag $K\beta_1$ — 61·2
	1	540·7	1863·2	N : Ag $K\beta_2$ — 11·8 (?)
	0–1	552·3	1942·0	(?)

(*a*) This band also contains F : $L\beta_1$ — M_{I}', M_{II}'.

79. GOLD (Element).

Level Values:	L_{I}	1060·2	M_{I}	252·9	N_{I}	58·0	O	7·8–0·8
	L_{II}	1014·4	M_{II}	235·1	N_{II}	49·1		
	L_{III}	878·5	M_{III}	202·8	N_{III}	42·8		
			M_{IV}	169·3	N_{IV}	26·4		
			M_{V}	163·0	N_{V}	25·0		
					N_{VI}	6·2		
					N_{VII}	5·8		

Emission Lines: $L\alpha_1$ ($M_V - L_{III}$) 715·5; $L\beta_1$ ($M_{IV} - L_{II}$) 843·0;
$L\beta_2$ ($N_V - L_{III}$) 853·5; $L\gamma_1$ ($N_{IV} - L_{II}$) 985·8;
Ll ($M_I - L_{III}$) 625·6.

Remarks.	Intensity.	rH.	ν/R.	Origin.
Inaccurate; doubtful line	1	243·5	385·3	F : Ll — 240·3 (M_{II}')
	1–2	249·4	404·1	
	1–2	254·6	421·0	F : Ll — 204·6 (M_{III}')
	2	260·7	441·3	F : $L\alpha_1$ — 274·2 (M_{I}' ?)
	2–3	269·1	470·0	F : $L\alpha_1$ — 245·5 (M_{II}')
	3	279·6	507·1	F : $L\alpha_1$ — 208·4 (M_{III}')
	2	285·6	529·0	
	5	289·3	542·7	F : $L\alpha_1$ — 172·8 (M_{IV}')
	2–3	290·9	548·6	F : $L\alpha_1$ — 166·9 (M_{V}')
	1	295·0	564·1	L_I : Ag $K\alpha_2$ — 1055·5
(*a*)	2–3	298·5	577·5	L_I : Ag $K\alpha_1$ — 1054·8
	2	307·1	611·0	L_{II} : Ag $K\alpha_2$ — 1008·6
(*a*)	3+	310·0	622·5	L_{II} : Ag $K\alpha_1$ -- 1009·8
	1–2	314·4	640·1	F : $L\beta_1$ — 202·9 (M_{III}')
	2	316·8	649·9	F : $L\beta_2$ — 203·6 (M_{III}'); $L\alpha_1$ — 65·6 (N′)
Not completely resolved (*b*)	3–4	323·4	677·0	F : $L\beta_1$ — 166·0 ($M_{IV,V}'$); $L\alpha_1$ — 38·5 (N′)
	3–4	326·7	690·7	F : $L\beta_2$ — 162·8 (M_{V}'); $L\alpha_1$ — 24·8 (N′)
	2	331·1	709·3	F : $L\alpha_1$ — 6·2 (N′, O′)
	1	332·9	716·9	
(*b*)	1	335·2	726·8	F : $L\gamma_1$ — 259·0 (M_{I}')
	3	339·1	743·6	L_{III} : Ag $K\alpha_2$ — 876·0
(*c*)	5–6	341·8	755·4	L_{III} : Ag $K\alpha_1$ — 876·9
Doubtful line	0–1	345·5	771·7	
	3—	348·0	782·8	L_I : Ag $K\beta_1$ — 1054·4; F : $L\gamma_1$ — 203·0 (M_{III}'); $L\beta_1$ — N′
	2	352·5	802·9	F : $L\beta_1$ — 40·9 (N′)
Not completely resolved	3–4	355·8	817·9	F : $L\gamma_1$ — 167·9 ($M_{IV,V}'$): $L\beta_1$ — N′
	3–4	358·0	827·9	L_{II} : Ag $K\beta_1$ — 1009·3; F : $L\beta_1$ — N′
	2	362·0	846·3	F : $L\beta_{2,3}$ — N′, O′
	1	365·4	862·1	L_{II} : Ag $K\beta_2$ — 1012·9
	0–1	367·5	871·9	
	1	375·9	911·8	
Not completely resolved	2	381·8	940·2	F : $L\gamma_1$ — N′

(*a*) to (*a*) F : $L\beta$ and Ll also in this region.

(*b*) to (*b*) A wide band exhibiting very complex structure. Components very imperfectly separated, and relative intensities difficult to estimate at all accurately.

(*c*) F : $L\gamma_1$ — M_{II}' also here.

79. GOLD (Element)—(continued).

Remarks.	Intensity.	*r*H.	*ν*/R.	Origin.
Head of a narrow band	4–5	386·2	961·8	L_{III} : Ag $K\beta_1$ — 875·4 ; F : $L\gamma_1$ — N′
	1–2	394·0	1000·5	L_{III} : Ag $K\beta_2$ — 874·5 : F : $L\gamma_2$ — N′, O′
	1	406·7	1065·1	
	0–1	418·6	1127·5	
	3	462·5	1372·0	M_I : Ag $K\alpha_2$ — 247·6
	5	464·9	1386·0	M_I : Ag $K\alpha_1$ — 246·3
	4+	468·0	1404·2	M_{II} : Ag $K\alpha_1$ — 228·1
Not completely resolved	4	471·0	1421·9	M_{III} : Ag $K\alpha_2$ — 197·7
	6	473·1	1434·4	M_{III} : Ag $K\alpha_1$ — 197·9
Narrow band	4–5	479·5	1472·8	$M_{IV, V}$: Ag $K\alpha_1$ — 159·5
(*d*)	5–6	497·0	1580·0	N : Ag $K\alpha_1$ — 52·3 ; Ag $K\alpha_2$ — 39·6
	5	498·7	1590·6	N_{III} : Ag $K\alpha_1$ — 41·7 ; M_I : Ag $K\beta_1$ — 246·6
	2	499·5	1595·6	N_V : Ag $K\alpha_2$ — 24·0
(*d*)	2–3	501·7	1609·4	N_V : Ag $K\alpha_1$ — 22·9
	3–4	506·1	1637·2	M_{III} : Ag $K\beta_1$ — 200·0
Narrow band	3	512·3	1676·6	$M_{IV, V}$: Ag $K\beta_1$ — 160·6 ; M_{III} : Ag $K\beta_2$ — 198·4
Narrow band	1–2	518·1	1714·0	$M_{IV, V}$: Ag $K\beta_2$ — 161·0
(*e*)	1	523·1	1746·5	
	1–2	529·6	1789·2	N : Ag $K\beta_1$ — 48·0
	0–1	531·6	1802·4	N : Ag $K\beta_1$ — 34·8
Narrow band	1	536·2	1833·0	N, O : Ag $K\beta_1$ — 4·2 ; Ag $K\beta_2$ — 42·0
	1+	545·2	1893·6	(?)
(*e*)	1	556·1	1968·1	(?)

(*d*) to (*d*). A narrow band, of complex structure.

(*e*) to (*e*). Outside the range of accurate measurement. A number of other faint lines and bands observed here, but on one or two plates only.

Note.—Photographs were taken with smaller magnetic fields, but no definite measurements could be made of the M fluorescent lines. This failure was mainly due to the heavy background of the low-velocity regions of the spectrum, and only in part to the low photographic efficiency of slow electrons. We have since obtained the M fluorescent lines of gold and other elements, by using a softer primary X-ray beam.

58. CERIUM (Oxide).

Level Values :					
L_I	483·3	M_I	106·2	N	21·7–8·5
L_{II}	454·1	M_{II}	94·6	O	3·2–2·5
L_{III}	421·9	M_{III}	88·1		
		M_{IV}	66·7		
		M_V	65·4		

Remarks.	Intensity.	*r*H.	ν/R.	Origin.
Doubtful line	0–1	395·0	1005·5	
Doubtful line	0–1	405·7	1060·1	
Not completely resolved	3–4	420·6	1138·1	L_I : Ag $K\alpha_2$ − 481·5
Not completely resolved	4+	423·1	1151·4	L_I : Ag $K\alpha_1$ − 480·9
Not completely resolved	3–4	425·9	1166·5	L_{II} : Ag $K\alpha_2$ − 453·1
Not completely resolved	4	428·5	1180·6	L_{II} : Ag $K\alpha_1$ − 451·7
Not completely resolved	3–4	432·4	1201·9	L_{III} : Ag $K\alpha_2$ − 417·7
	4	434·8	1215·0	L_{III} : Ag $K\alpha_1$ − 417·3
Narrow band	1	444·6	1269·5	
Doubtful line	1	451·9	1310·8	
	2	460·2	1358·6	L_I : Ag $K\beta_1$ − 478·6
	1–2	464·8	1385·4	L_{II} : Ag $K\beta_1$ − 451·8
	1	470·8	1420·8	L_{III} : Ag $K\beta_1$ − 416·4
	1	480·6	1479·3	
Not completely resolved ; inaccurate	6	489·4	1532·9	M : Ag $K\alpha_1$ − 99·4 ; Ag $K\alpha_2$ − 86·7
	3–4	492·0	1549·0	M : Ag $K\alpha_1$ − 83·3
Not completely resolved	4–5	500·8	1603·7	N : Ag $K\alpha_2$ − 15·9 ; Ag $K\alpha_1$ − 28·6
Not resolved completely	4	503·5	1620·7	N : Ag $K\alpha_1$ − 11·6 ; $K\alpha_2$ − (N′, O′)
Head of a band	2	505·1	1630·9	O : Ag $K\alpha_1$ − 1·4
	2	522·1	1740·0	M : Ag $K\beta_1$ − 97·2
	1	532·9	1811·0	N : Ag $K\beta_1$ − 26·2
Doubtful line	0–1	549·9	1925·6	(?)

Note.—Not a very good set of photographs.

47. SILVER (ELEMENT).

Level Values :				
L_I 280·9	M_I 52·8	N 6·9–0·4
L_{II} 259·9	M_{II} 44·8	
L_{III} 246·8	M_{III} 42·6	
	M_{IV} 27·4	
	M_V 27·0	

Remarks.	Intensity.	*r*H.	ν/R.	Origin.
Doubtful line	1	407·7	1070·3	
Doubtful line	1	415·9	1113·2	
Doubtful line	0–1	420·6	1138·0	
Doubtful line	0–1	426·3	1168·7	
Doubtful line	0–1	432·8	1204·1	
Doubtful line	0–1	439·2	1239·3	
	1–2	451·1	1306·3	
Not completely resolved	3–4	457·2	1341·3	L_I : Ag $K\alpha_2 - 278\cdot3$
	6	459·3	1353·5	L_I : Ag $K\alpha_1 - 278\cdot8$
	2–3	460·8	1362·0	L_{II} : Ag $K\alpha_2 - 257\cdot6$
Not completely resolved	3–4	463·1	1375·4	L_{II} : Ag $K\alpha_1 - 256\cdot9$; L_{III} : Ag $K\alpha_2 - 244\cdot2$
	2–3	465·2	1387·8	L_{III} : Ag $K\alpha_1 - 244\cdot5$
Head of a narrow band	2	474·6	1443·3	
	1	483·5	1497·0	
	3	493·6	1558·9	L_I : Ag $K\beta_1 - 278\cdot3$
Head of a narrow band (*a*)	5	497·7	1584·3	M : Ag $K\alpha_1 - 48\cdot0$
	2–3	499·4	1595·0	M : Ag $K\alpha_1 - 37\cdot3$; L_{III} : Ag $K\beta_1 - 242\cdot2$
Head of a narrow band	3	504·9	1629·5	N : Ag $K\alpha_1 - 2\cdot8$
	2	511·8	1673·4	
	1	517·0	1706·9	
Doubtful line	1	521·7	1737·4	
Narrow band	1–2	530·3	1793·8	M : Ag $K\beta_1 - 43\cdot4$

(*a*) Band includes Ag $K\beta_1 - L_{II}$.

Note.—All this set taken with Schumann plates ; fainter lines and intensities not altogether reliable.

42. MOLYBDENUM (Element).

Level Values : K 1473·4 L_I 211·9 M_I 37·3 N 4·7–0·2
L_{II} 193·4 M_{II} 31·1
L_{III} 185·8 M_{III} 29·8
M_{IV} 17·1
M_V 16·9

Emission Lines : $K\alpha_1$ (L_{III} — K) 1287·5 ; $K\alpha_2$ (L_{II} — K) 1279·7 ;
$K\beta_1$ (M_{III} — K) 1443·6 ; $K\beta_2$ ($N_{II,\,III}$ — K) 1470·5.

Remarks.	Intensity.	*r*H.	*ν*/R.	Origin.
Doubtful line …………………	0–1	402·2	1042·0	F : [K — 2 L_I — 7·6]
Not completely resolved (*a*)	4	407·4	1068·8	F : $K\alpha_1$ — 218·7 ; $K\alpha_2$ — 210·9 (L_I')
	6	410·9	1087·0	F : $K\alpha_1$ — 200·5 (L_{II}') ; $K\alpha_2$ — 192·7
	3	412·4	1094·8	F : $K\alpha_1$ — 192·7 (L_{III}') ; $K\alpha_2$ — 184·9
(*a*)	2	413·7	1101·6	F : $K\alpha_1$ — 185·9 (L_{III}')
	2–3	437·7	1231·1	F : $K\beta_1$ — 212·5 (L_I')
Narrow band …………………	5	442·4	1257·2	F : $K\beta_1$ — 186·4 (L_{III}') ; $K\alpha_1$ — 30·3 (M′)
	2–3	447·1	1283·5	F : $K\alpha_1$ — 4·0 (N′)
Narrow band ; doubtful ….	1	452·8	1316·0	
Doubtful line …………………	1	459·4	1354·0	
Not completely resolved ; intensity uncertain …….	5	468·5	1407·1	L_I : Ag $K\alpha_2$ — 212·5 ; F : $K\beta_1$ — 36·5 (M′)
	6	470·8	1420·8	L_I : Ag $K\alpha_1$ — 211·5 ; F : $K\beta_1$ — 22·8 (M′)
	3–4	475·4	1448·1	$L_{II,\,III}$: Ag $K\alpha_1$ — 184·2
	1–2	479·0	1469·8	F : $K\beta_2$ — 0·7 (N′) (?)
Narrow band …………………	1	481·5	1484·8	
	1	487·5	1521·3	
Doubtful line …………………	0–1	491·3	1544·6	
	3	499·5	1595·6	M : Ag $K\alpha_1$ — 36·7
	2–3	503·8	1622·6	L_I: Ag $K\beta_1$ — 214·6 ; Ag $K\alpha_1$ — M (?)
	1	508·0	1649·2	$L_{II,\,III}$: Ag $K\beta_1$ — 188·0.

(*a*) to (*a*) Evidence of unresolved detail in this band, and in the corresponding bands of the elements in the following tables.

40. ZIRCONIUM (Oxide).

Level Values :			
K 1325·7	L_I 187·7	M_I 31·8	N 3·8–0·3
	L_{II} 169·8	M_{II} 26·5	
	L_{III} 163·9	M_{III} 25·5	
		$\left.\begin{matrix}M_{IV}\\M_V\end{matrix}\right\}$ 13·4	

Emission Lines : $K\alpha_1$ (L_{III} — K) 1161·9 ; $K\alpha_2$ (L_{II} — K) 1155·7 ; $K\beta_1$ (M_{III} — K) 1300·9 ; $K\beta_2$ ($N_{II, III}$ — K) 1323·8.

Remarks.	Intensity.	*r*H.	ν/R.	Origin.
(*a*)	2	212·6	294·0	K : Ag $K\alpha_2$ — 1325·6
(*a*)	3	217·2	306·8	K : Ag $K\alpha_1$ — 1325·5
Doubtful line	0–1	275·0	490·7	
	1–2	280·6	510·7	K : Ag $K\beta_1$ — 1326·5
	0–1	285·2	527·5	
Doubtful line	1–2	296·4	569·4	
Doubtful line	1–2	316·3	647·8	
Doubtful line	1	333·0	717·3	
Uncertain : not fully resolved	2–3	385·6	958·8	F : $K\alpha_1$ — 203·1 ; $K\alpha_2$ — 196·9 (L_I')
Uncertain ; not fully resolved	2–3	387·2	966·7	F : $K\alpha_1$ — 195·2 ; $K\alpha_2$ — 189·0 (L_I')
Head of a band	6	390·6	983·5	F : $K\alpha_1$ — 178·4 ; $K\alpha_2$ — 172·2 (L_{II}')
	1	392·1	991·0	F : $K\alpha_1$ — 170·9 ; $K\alpha_2$ — 164·7 (L_{II}', L_{III}' ?)
	1	393·8	999·5	F : $K\alpha_1$ — 162·4 (L_{III})
(*b*)	2–3	414·8	1107·4	F : $K\beta_1$ — 193·5 (L_I')
Head of a band	5	419·7	1133·3	F : $K\beta_1$ — 167·6 (L_{III}') ; $K\alpha_1$ — 28·6 (M′)
Narrow band	1–2	423·9	1155·7	F : $K\alpha_1$ — 4·2 (N′)
(*b*)	1–2	444·8	1270·6	F : $K\beta_1$ — 30·3 (M′)
Not completely resolved	3	472·5	1430·9	L_I : Ag $K\alpha_2$ — 188·7
	5–6	474·8	1444·5	L_I : Ag $K\alpha_1$ — 187·8
Not completely resolved	3	477·9	1463·2	L_{II} : Ag $K\alpha_1$ — 169·1
	2–3	479·1	1470·3	L_{III} : Ag $K\alpha_1$ — 162·0
Head of a narrow band	3	500·8	1603·7	M : Ag $K\alpha_1$ — 28·6
(*c*)	2	505·2	1631·4	N : Ag $K\alpha_1$ — 0·9
	2–3	508·2	1650·4	L_I : Ag $K\beta_1$ — 186·8
	1–2	511·1	1669·0	L_{II} : Ag $K\beta_1$ — 168·2
	1–2	512·5	1677·9	L_{III} : Ag $K\beta_1$ — 159·3
(*c*)	0–1	513·7	1685·6	L_I : Ag $K\beta_2$ — 189·4
Doubtful line	1	531·5	1801·7	M : Ag $K\beta_1$ — 35·5
	0–1	537·7	1843·0	M : Ag $K\beta_2$ — 32·0
	0–1	546·0	1899·0	(?)
	0–1	557·3	1976·4	(?)

(*a*) to (*a*) Numerical agreement here is fortuitous ; *r*H 212·6 is the mean of rather discordant measurements ± 0·3 gauss cm. approx.).

(*b*) to (*b*) *Cf.* IV, p. 291. These lines were not measured in the earlier work, as they fall in the region MoK—ZrL, M. The latter (secondary lines) were picked out in the 1926 photographs by suppressing the general radiations as far as possible.

(*c*) to (*c*) A wide band with rather complex structure ; intensities of individual components very difficult to estimate.

38. STRONTIUM (Oxide).

Level Values : K 1186·0 L_I 163·6 M_I 26·7 N 3·2–1·9
L_{II} 147·9 M_{II} 21·0
L_{III} 143·2 M_{III} 20·2
$\left.\begin{matrix}M_{IV}\\M_V\end{matrix}\right\}$ 10·2

Emission Lines : $K\alpha_1$ (L_{III} — K) 1043·4 ; $K\alpha_2$ (L_{II} — K) 1038·4 ;
$K\beta_1$ (M_{III} — K) 1166·0 ; $K\beta_2$ ($N_{II,\,III}$ — K) 1184·7.

Remarks.	Intensity.	*r*H.	ν/R.	Origin.
	2–3	258·5	433·9	K : Ag $K\alpha_2$ — 1185·7
	3–4	262·2	446·3	K : Ag $K\alpha_1$ — 1186·0
	2	317·1	651·1	K : Ag $K\beta_1$ — 1186·1
	1	363·4	852·8	F : [K — 2 L_I — 6·0]
	3	367·1	870·0	F : $K\alpha_1$ — 173·4 ; $K\alpha_2$ — 168·4 (L_I')
	6	371·1	888·9	F : $K\alpha_1$ — 154·5 ; $K\alpha_2$ — 149·5 ($L_{II,\,III}'$)
Doubtful line (*a*)	1	372·1	893·6	F : $K\alpha_1$—149·8 ; $K\alpha_2$—144·8 ($L_{II,\,III}'$?)
	3	397·6	1018·7	F : $K\alpha_1$— 24·7 (M′) ; $K\beta_1$— 147·3 (L_{III}')

(*a*) Appears on only one of four plates.
Note.—Poor set of photographs. Many other lines rejected for lack of confirmation.

33. ARSENIC (Oxide).

Level Values : K 874·0 L_I ca. 114* M 14·9–3·0
L_{II} 100·0
L_{III} 97·4

Emission Lines : $K\alpha_1$ (L_{III} — K) 776·6 ; $K\alpha_2$ (L_{II} — K) 774·0 ;
$K\beta_1$ (M_{III} — K) 863·6 ; $K\beta_2$ ($N_{II,\,III}$ — K) 873·8.

Remarks.	Intensity.	*r*H.	ν/R.	Origin.
	1–2	300·8	586·3	
	1–2	314·3	639·7	F : [K — 2 L_I — 6·3]
Not completely resolved	3	318·6	657·2	F : $K\alpha_1$ — 119·4 ; $K\alpha_2$ — 116·8 (L_I')
	6	322·4	672·8	F : $K\alpha_1$ — 103·8 ; $K\alpha_2$ — 101·2 ($L_{II\ III}'$)
Narrow band ; doubtful	1–2	330·4	706·3	
Doubtful line	1	334·5	723·8	
(*a*)	4	339·5	745·4	K : Ag $K\alpha_2$ — 874·2 ; F : $K\beta_1$ — 118·2 (L_I')
(*b*)	5–6	343·0	760·6	F : $K\alpha$ — M′ ; $K\beta_1$ — 103·0 ($L_{II,\,III}'$)
(*a*)	1	344·3	766·4	F : $K\alpha$ — M′ ; $K\beta_1$ — 97·2 (L_{III}')
	1	362·3	847·7	F : $K\beta_1$ — 15·9 (M′)
	0–1	365·7	863·5	F : $K\beta_1$ — 0·1 ; $K\beta_2$ — 10·3 (M′)
	1–2	382·2	942·2	
	3	386·7	964·2	K : Ag $K\beta_1$ — 873·0

Note.—A fairly good set of plates, but all Schumann. Fainter lines and intensities therefore somewhat uncertain.
(*a*) to (*a*) Complex band showing unresolved structure.
(*b*) This part of band also contains Ag $K\alpha_1$ — As K.
* *Cf.* Mukherjee and Ray, ‘ Zeits. f. Physik,’ vol. 57, p. 345 (1929).

29. COPPER (Element).

Level Values : K 661·5 L_I ca. 81–82* M 8·8–0·4
L_{II} 70·3
L_{III} 68·8

Emission Lines : $K\alpha_1$ ($L_{III} - K$) 592·8 ; $K\alpha_2$ ($L_{II} - K$) 591·3 ;
$K\beta_1$ ($M_{III} - K$) 655·9 ; $K\beta_2$ ($N_{II,\,III} - K$) 661·3.

Remarks.	Intensity.	*r*H.	ν/R.	Origin.
Doubtful line	0–1	258·5	433·9	
Not completely resolved	3	279·8	507·9	$F : K\alpha_1 - 84{\cdot}9\ (L_I')$
	6	282·8	518·7	$F : K\alpha_1 - 74{\cdot}1\ (L_{II,\,III}')$
Doubtful line (*a*)	0–1	284·3	524·2	$F : K\alpha_1 - 68{\cdot}6\ (L_{III})$
Not completely resolved ; inaccurate	2	297·6	574·0	$F : K\beta_1 - 81{\cdot}9\ (L_I')$
	3–4	300·7	585·9	$F : K\alpha_1 - 6{\cdot}9\ (M')$; $K\beta_1 - 70{\cdot}0\ (L_{II,\,III}')$
	1	316·8	649·9	$F : K\beta_1 - 6{\cdot}0\ (M')$
	3–4	385·6	958·8	$K : Ag\ K\alpha_2 - 660{\cdot}8$
	5–6	388·3	972·1	$K : Ag\ K\alpha_1 - 660{\cdot}2$
Doubtful line	0–1	421·5	1142·9	
	3	427·9	1177·3	$K : Ag\ K\beta_1 - 659{\cdot}9$
Doubtful line	0–1	434·9	1215·6	$K : Ag\ K\beta_2 - 659{\cdot}4$
Doubtful line	0–1	467·5	1401·2	
Doubtful line	0–1	479·4	1472·1	
	2	490·7	1541·0	$L_I : Ag\ K\alpha_2 - 78{\cdot}6$
	3–4	493·0	1555·2	$L_I : Ag\ K\alpha_1 - 77{\cdot}1$
Doubtful line	1	497·0	1580·0	
Narrow band	1–2	504·2	1625·1	$M : Ag\ K\alpha_1 - 7{\cdot}2$
	2	525·2	1759·9	$L_I : Ag\ K\beta_1 - 77{\cdot}3$
	0–1	530·7	1796·4	$L_I : Ag\ K\beta_2 - 78{\cdot}6$
	1	535·5	1828·3	$M: Ag\ K\beta_1 - 8{\cdot}9$
Very doubtful line	0–1	546·9	1905·1	(?)
Very doubtful line	0–1	556·7	1972·2	(?)

(*a*) On one plate only ; possibly due to "external" absorption.
* *Cf.* Mukherjee and Ray, *loc. cit.*

§ 3. *Accuracy of Results.*

It will be seen from § 2 that we have appreciably extended the measurements of both the secondary and the fluorescent lines, and that improved technique has brought out a great deal of new detail in the corpuscular spectra. In other respects the new work is less satisfactory ; it has been carried on, over a period of about 2 years, under unusually exasperating conditions, while the only available room in the laboratory was undergoing a necessary process of complete re-equipment and partial reconstruction. The details of the resulting annoyances are of purely domestic interest, but we are compelled to make reference to their effect on the accuracy of the work. For long periods experiments could be conducted neither continuously nor systematically, and many series had to be abandoned at an incomplete stage, to make way for building operations. For this reason, although recalibration was naturally resorted to after every obvious upheaval or suspected interference, the results are less accurate and complete than they would have been under more normal working conditions. They are sufficiently accurate for the purpose of the present survey, but it is possible that many of the rH values quoted in § 2 may be in error by as much as 1 part in 500.

In spite of this, the results have been tabulated as they were first calculated, *i.e.*, to the nearest 0·1 in rH and ν/R. This is justifiable to some extent, as the small differences between the energies of neighbouring lines are subject to much smaller absolute errors than are the energies themselves, and such differences are frequently of importance.

In this connection, it may be mentioned that an error in rH of 0·1 gauss cm. corresponds fairly well to the average error in a single measurement of the position of a clearly separated line on a good plate, *i.e.*, as distinct from systematic errors which might be caused by errors of adjustment or displacements of the field coils. Further, it may be advisable to point out that an absolute error of 1 part in 1,000 in the larger rH values means an error of about 3 or 4 Rydberg units in the next column—say, about 40 electron-volts in the equivalent energy.

The absolute errors are probably greatest for the lines of highest energy, as there is a troublesome correction for the effect of the stray field of the compensating coils (II, p. 460), which becomes serious for paths of small curvature. We are now using a re-designed X-ray tube, which requires no compensating coils, but all the results now under discussion were obtained with the older disposition.

§ 4. *Relative Intensities of the Secondary Cathode Ray Groups.**

In the figure we have represented a selection of relative intensities, including some from previous papers (II, III, IV). The figure, which is self-explanatory, shows how the new results link up with the older sets. It makes unnecessary any detailed verbal description of the general run of the intensities with different primary X-ray frequencies.

These intensities have already (II, III, IV) been discussed at some length, particularly in relation to the remarkable variation with ν_0, the primary X-ray frequency, of the individual lines within a given group. Fairly extensive data are now available in the L and M groups ; the N levels remain largely unexplored, but here again there is some evidence of the existence of the same effect.

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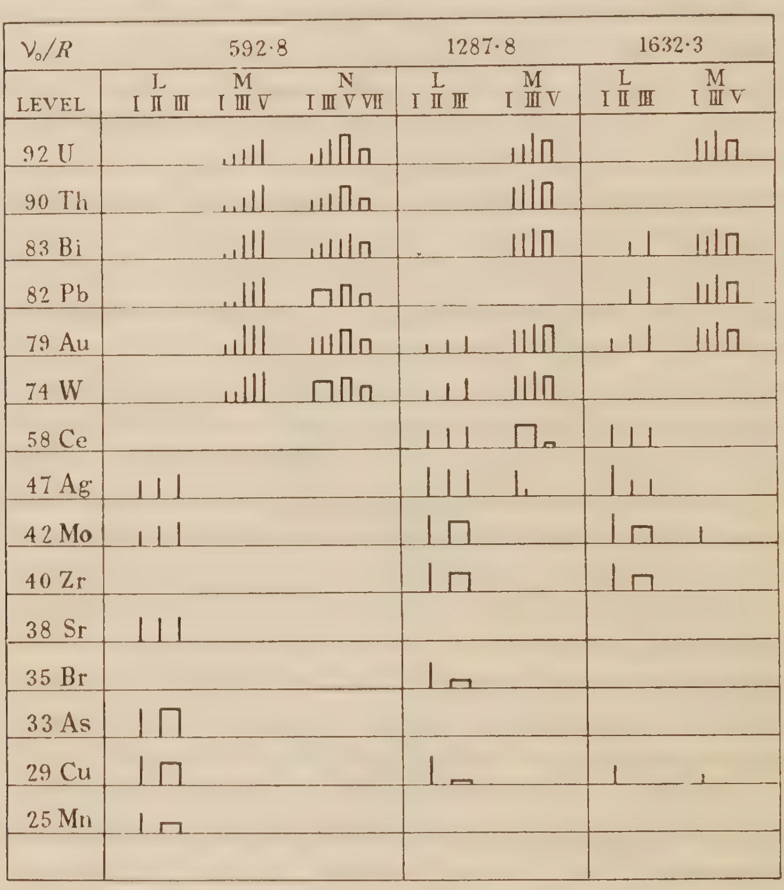
* [*Note added in proof, May* 19, 1930—In connection with § 4, reference may be made to a paper by G. Schur, 'Ann. Physik,' vol. 4, p. 433 (1930)—one of a series of three theoretical papers on the photo-effect from Professor Sommerfeld's Department in Munich. This number of the 'Annalen' was not received here until April 7th.]



Relative Intensities of Secondary Cathode Ray Groups with different Primary X-ray Frequencies.

Briefly, the effect is that lines corresponding to levels of smaller azimuthal quantum number k_1,* which are relatively weak when the primary radiation is just hard enough to excite all members of a group, become relatively more intense with increasing ν_0 ; when ν_0 is very much greater than the mean critical excitation frequency of, say, the three L sub-groups, L_{II} and L_{III} are almost entirely suppressed in favour of L_I (see, for example, 29 Cu in fig. 1: the level values are $L_I = 81$, $L_{II} = 70$, $L_{III} = 69$ Rydberg units). This effect—originally surmised from observations with a single primary frequency operating on a number of different targets, covering a suitable range of atomic numbers—has now been established over the range 600 to 1600 ν/R. Experiments now in progress (with Dr. R. T. Dunbar) are extending the work to regions of lower frequency. The difficulties here are the greater absorbability of the X-rays and the feebler photographic action of the photoelectrons, but these have already been to some extent overcome.

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* In the usual (n_{k_1, k_2}) notation for X-ray levels.

We have no definite evidence of similar variations in the relative intensities of the partners in the "spin" doublets (L_{II}, L_{III}), (M_{II}, M_{III}), (M_{IV}, M_V), though our results do not absolutely preclude them. Such variations would be difficult to detect, owing to the dependence of the spin doublet separation on the fourth power of the effective atomic number. With the heavier elements, the separations of many of these doublets are too great for the accurate comparison of intensities, while with diminishing atomic number the resolving power of the apparatus falls off rapidly, exactly in the regions where any such effect would most naturally be sought.

These relative intensities are of cardinal importance in relation to the general problem of the interaction of X-rays and matter, as they clearly cannot be accommodated in any classical or quasi-classical theory of absorption. There is also on the radioactive side a body of experimental evidence which suggests that the classical absorption formulæ quite definitely break down when they are extrapolated to very short wave-lengths.

In both these respects new wave-mechanical theories of absorption, developed independently by Wentzel and by Oppenheimer,* appear to offer the basis of a satisfactory solution. Unfortunately, the general validity of the new formulæ cannot yet be accurately assessed, in spite of the number and accuracy of existing absorption data in K and L ranges. The direct absorption measurements do not furnish a very sensitive test of theory, especially when due allowance is made (as has not invariably been done) for the flexibility of "constants" which at the present stage remain somewhat widely adjustable. As regards the problem of our relative intensities, however, the new theories do definitely predict variations in the relative absorbing powers of the different electronic groups, precisely in the required sense. In Wentzel's treatment this appears explicitly in the form of a factor $(Z^2\lambda)^{k_1-1}$ in the contribution of a group to the total atomic absorption coefficient—which is, so far as can be seen at present, in very fair accord with the experimental results (Wentzel, *loc. cit.*).

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* Wentzel, 'Z. Physik,' vol. 40, p. 574 (1927); Oppenheimer, *ibid.*, vol. 41, p. 268 (1927).

We hope that it may in time be practicable to put the intensity measurements on a sounder quantitative basis. Our estimates are still subjective, although in some instances (III, IV) they have been compared with the readings of the photoelectric microphotometer. So far this has been possible only with the stronger lines, and even with instrumental observation there are difficulties arising from the structure of the lines. We have recently (since the completion of the series of experiments now under discussion) succeeded in improving the photographic technique to an extent which suggests that even the fainter lines may be brought within the scope of photometric examination. We cannot at the moment contemplate carrying out such tests on a sufficiently wide scale, but meanwhile we have obtained some confirmation of the general reliability of our visual estimates by a simple but effective method based on the comparison of photographs taken with "mixed" targets. Two elements are chosen which give strong lines in the same region of the photographic plate, and photographs are taken with targets containing different proportions of the elements. Simple inspection of a set of plates gives a very fair control of estimates of relative intensity of neighbouring lines. The method clearly has an application to the comparison of partial absorption coefficients of all levels of similar binding energy,* but so far we have not had the necessary leisure for its full development.

In connection with these interpretations of our results, some guarantee is naturally required that our intensities shall be representative of the partial absorptions of the respective levels—especially in view of recent important work from the Pasadena Laboratory; there Watson and van den Akker,† using a modified magnetic spectrograph designed by Watson,‡ have shown that the distribution of the photoelectrons about the primary X-ray beam is markedly dependent on the azimuthal quantum number of the level of origin, and definitely, though less markedly, upon the binding energy. In our work, we take the photoelectrons making angles of roughly 80° to 90° with the direction of the primary beam (the angles indicated as generally suitable by Watson's earlier work); from the information given by Watson and van den Akker, and from our own observations with targets of varying thickness, it appears certain that our targets are in all cases sufficiently thick to give practical, if not complete, isotropy by scattering. Our intensities are therefore fairly representative of the integrated photoelectric emissions over all angles of ejection.

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* Robinson and Young, 'Nature,' vol. 123, p. 203 (1929).

† Watson and van den Akker, 'Roy. Soc. Proc.,' A, vol. 126, p. 138 (1929). We are indebted to Prof. Watson for communicating some of the results to us at an early stage, and for some very beautiful photographs showing these effects.

‡ 'Phys. Rev.,' vol. 30, p. 479 (1927).

§ 5. *The Fluorescent Lines.*

It will be seen from § 2 that we have extended the fluorescent spectra of some of the elements already treated in IV—the use of a harder primary beam allowing regions to be investigated which were, in the earlier work, obscured by overlapping secondary lines. In addition, we have examined several other spectra, especially those arising from internal K conversions. There are some points of general interest which will be briefly dealt with.

In the first place, it is clear from § 2 that the majority of the stronger fluorescent lines can be not unreasonably attributed to internal conversions, in slightly modified levels of the normal atom, of the stronger characteristic ("fluorescent") X radiations of the target. The energy differences between the normal X-ray levels and the accented levels shown in § 2 are of the type which would be expected in atoms which were left doubly ionised. Although these energy differences cannot yet be computed from theory, it is not difficult to fix them approximately, between fairly narrow limits. In this way, Wentzel,* and more recently Druyvesteyn,† have successfully explained a number of the satellites on the high-frequency side of the normal X-ray lines (Wentzel's X-ray "spark" lines). Again, Ellis and Wooster‡ have pointed out that whole ranges of β-ray spectra can be very well described in terms of a straightforward "internal absorption" of γ rays, following in many respects the known laws of "external absorption" of quantum radiations. The two problems are by no means identical, but they possess sufficient general similarity to indicate that this simple conception will explain qualitatively and even to some extent quantitatively a great deal of the experimental material. It is, however, clearly inadequate to account for all the details either of the non-diagram X-ray lines or of our fluorescent corpuscular spectra (*cf.* IV, p. 300).

Our new results bring out a further difference between external and "internal" absorption or conversion: it will be seen that in several instances we have recorded fluorescent lines whose energy can be most simply represented by (ν/R) $(K - 2L_I{}')$, *i.e.*, by the process $L_I - K$, $L_I - \infty$, although $L_I - K$ is a forbidden transition in the series scheme. There is no very well authenticated report of the appearance of the corresponding line ($K\alpha_3$?) in emission spectra, and there can be no suggestion that it would be sufficiently intense to be recorded by its secondary electrons. On the other hand, Wentzel,* who has given an elegant wave-mechanical treatment of the problem, suggests that this fluorescent line should appear as the result of radiationless transitions, though with appreciably smaller intensity than lines like $(K - 2\,L_{II,\,III})$. In § 2 we have indicated the line in question by square brackets [ ]; it is neither very intense nor very well separated—there is a great deal of unresolved structure in the K — L fluorescent groups—but there can be no doubt of its existence, though there may be of its interpretation.

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* 'Ann. Physik,' vol. 66, p. 437 (1921), and vol. 73, p. 647 (1924).

† 'Z. Physik,' vol. 43, p. 707 (1927); Groningen Dissertation, "Het Röntgenspectrum van de 2de soort" (1928).

‡ 'Roy. Soc. Proc.,' A, vol. 114, p. 276 (1927).

The question is complicated by the way in which the X-ray term structure is modified by the removal of a second electron (Pauli's reciprocity rule†). Experimental evidence of the splitting of the terms has been brought forward by, among others, Coster, Druyvesteyn, van der Tuuk (literature in van der Tuuk, 'Groningen Dissertation,' 1928). Thus, although experimentally it is clear that the doubly ionised atom generally retains some close similarity with the singly ionised atom—in the sense that levels can be recognised which correspond fairly closely with the normal X-ray terms—it is quite illogical to speak of the "removal of a second electron from the same level." In classifying the fluorescent lines we continually imply the occurrence of processes of this and similar types; in this we are justified solely in so far as we can avoid excessive circumlocution by speaking in terms of the older, semi-mechanical picture of electron levels.

The detailed examination of the fluorescent corpuscular spectra, with our improving technique in resolving complex bands and detecting faint lines, is very likely to throw further light on this particular problem. It appears in fact to be the most direct method available, and to be free from many of the difficulties which attend the X-ray spectroscopy of the corresponding emission lines.

§ 6. *General.*

We have already (§§ 1, 3) touched upon difficulties which arise in the comparison of electronic and X-ray energies. These are comparatively unimportant in the case of the secondary cathode ray groups, as there is never any serious difficulty in identifying a level. They appear, however, in an aggravated form in the work on the fluorescent lines, where we are concerned with the measurement of relatively small differences from normal levels. The only satisfactory method of comparison here is to measure both the normal and modified levels in the same way, and under conditions as nearly identical as possible.

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* 'Z. Physik,' vol. 43, p. 524 (1927).

† Pauli, 'Z. Physik,' vol. 31, p. 765 (1925); see also an earlier paper by Wentzel, *ibid.*, p. 445.

We shall, therefore, as soon as possible, carry out experiments on this plan, comparing directly, for instance, the L fluorescent lines of gold with the secondary lines produced in a gold target by a primary beam of gold L radiations. This will be done entirely with the same apparatus, thus eliminating in one step all possible sources of systematic error. The work already completed (IV and the present paper) may be taken as a general survey of typical fluorescent corpuscular spectra. We do not propose at the moment to continue it, as it seems clear that a stage has been reached when the work can be more usefully directed towards the detailed study of a few selected elements, controlled in the manner just indicated.

We are at the moment engaged on subsidiary experiments which have been suggested by our observation, in the present work, of a number of lines of doubtful origin, which are clearly not fluorescent lines. Some of these might possibly be attributed to the effects of simultaneous double ionisation of the atom by the direct absorption of a single quantum of X radiation. Processes of this kind are now frequently invoked to explain the structure of absorption edges ; it will be a matter of considerable interest to see how far the corpuscular spectra can produce evidence of their occurrence—especially as it is not clear how the balance of energy would be expected to apportion itself over the two photoelectrons.

In photographs taken with fairly hard primary X-rays it is difficult to be quite confident of the reality of faint corpuscular lines—in part because of the complexity of the resulting secondary and fluorescent spectra, and in a larger part because of the intense continuous background produced by scattered and straggled electrons. There is always a possibility of purely instrumental effects producing gradations in the continuous background which can be mistaken for faint lines ; with slow electrons this can be checked by varying the magnetic field, but with faster ones we are working too near the maximum steady field of which the apparatus is capable, to be able to use this control effectively. We have therefore been obliged to reject a number of observations of faint lines, for lack of satisfactory confirmation.

For these reasons we are carrying out a short series with relatively soft X-rays, in a systematic search for lines resulting from multiple ionisation. When this has been completed, we hope to proceed at once to the closer examination of the fluorescent lines.

We are indebted to the Government Grant Committee of the Royal Society for grants in aid of this work; to Dr. R. T. Dunbar, who has been working on allied problems, and who has aided us in arriving at a satisfactory photographic technique for parts of this work; and to Mr. E. Holden, who has made a great deal of the apparatus.

The Scattering of α-Particles in Helium.

By J. Chadwick, F.R.S.

(Received April 8, 1930.)

§ 1. The problem of the collision of two particles which act upon each other with forces varying as the inverse square of the distance between them has been solved exactly on the basis of the new quantum mechanics, and the solution is the same as that given by classical mechanics. In a recent paper, however, Mott* has pointed out that this agreement between the predictions of classical mechanics and wave mechanics depends upon the dissimilarity of the colliding particles; if the particles are identical the scattering laws given by the wave mechanics will be very different from those of classical theory.

Mott has considered the two types of collision between similar particles, (1) in which the particles possess spin, such as the collisions of electrons with electrons or protons with hydrogen nuclei, and (2) in which the particles have no spin, such as the collisions of α-particles with helium nuclei.

In the latter case the argument may be put in a general way as follows. If a narrow pencil of α-particles is passed through helium the particles which travel in a direction θ to the pencil will consist of scattered α-particles and projected helium nuclei, the latter corresponding to the α-particles scattered through $\frac{1}{2}\pi - \theta$. Neglecting for the moment the motion of the centre of gravity of the system of colliding particles, the numbers of scattered α-particles and projected helium nuclei proceeding in direction θ will be proportional to $\operatorname{cosec}^4 \frac{1}{2}\theta$ and $\operatorname{cosec}^4 \frac{1}{2}(\pi - \theta)$ respectively. If we represent these two streams of particles by waves, they will have amplitudes proportional to $\operatorname{cosec}^2 \frac{1}{2}\theta$ and $\operatorname{cosec}^2 \frac{1}{2}(\pi - \theta)$. Now the band spectrum of the helium molecule shows that the helium nucleus has no spin, and thus the scattered α-particles and the projected helium nuclei which travel in the same direction will not only have the same velocity but will be identical in all respects. If we cannot by any possible experiment distinguish between a scattered α-particle and a helium nucleus of the same velocity, the two waves will interfere and give a wave of amplitude

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* Mott, 'Roy. Soc. Proc.,' A, vol. 126, p. 259 (1930).

$$e^{i\alpha_1} \operatorname{cosec}^2 \tfrac{1}{2}\theta + e^{i\alpha_2} \operatorname{cosec}^2 \tfrac{1}{2}(\pi - \theta)$$

where α_1 and α_2 are phase factors.

The intensity of the scattered + projected beam in a direction θ is given by the square of the amplitude of the wave, or

$$\operatorname{cosec}^4 \tfrac{1}{2}\theta + \operatorname{cosec}^4 \tfrac{1}{2}(\pi - \theta) + 2 \operatorname{cosec}^2 \tfrac{1}{2}\theta \,.\, \operatorname{cosec}^2 \tfrac{1}{2}(\pi - \theta) \,.\, \cos(\alpha_1 - \alpha_2).$$

Allowing now for the motion of the centre of gravity of the system in collision this becomes

$$\operatorname{cosec}^4 \theta + \operatorname{cosec}^4 (\tfrac{1}{2}\pi - \theta) + 2 \operatorname{cosec}^2 \theta \,.\, \operatorname{cosec}^2 (\tfrac{1}{2}\pi - \theta) \,.\, \cos(2n \log \tan \theta)$$

when the value of $\cos(\alpha_1 - \alpha_2)$ is introduced.

$n = E^2/hV$, where E, V are the charge and velocity of the incident α-particle.

On the classical theory, the first term represents the number of scattered α-particles, and the second term the number of projected helium nuclei, while the third term does not occur.

The ratio of the quantum theory scattering to the classical scattering is shown for different values of n, or different initial velocities of the α-particle, in fig. 1. The ratio has a maximum value of 2 at 45°, for all velocities of the α-particle, and then falls to unity when $\cos(2n \log \tan \theta) = 0$, or $2n \log \tan \theta = \pm \pi/2$. For smaller angles than that given by this relation the ratio oscillates around unity, being equal to 1 when $2n \log \tan \theta = \pm 3\pi/2, \pm 5\pi/2$, etc. Curves 1, 2, and 3 are drawn for α-particles of velocity $1 \cdot 92 \times 10^9$ cm. per second, 1×10^9, and 5×10^8, corresponding to ranges in air of 7 cm., 1·3 cm., and about 0·2 cm. respectively. As the velocity of the α-particle decreases the hump at 45° becomes narrower and the oscillations at small and large angles more pronounced.

It is clear that a test of this application of the new mechanics can be most simply obtained by examining the scattering of α-particles in the neighbourhood of 45°. In the experiments of Rutherford and Chadwick on the scattering of α-particles in helium the predicted effect is not apparent, for in the collisions studied there the forces between the particles were due mainly to their structure and only with slow α-particles did the scattering agree even roughly with that calculated on Coulomb forces. In the experiments described in this paper observations of scattering in helium have been made with α-particles of much lower velocity than those used in the previous experiments, and it has been found that the amount of scattering at 45° is twice that expected on classical theory, as predicted by Mott's calculations.

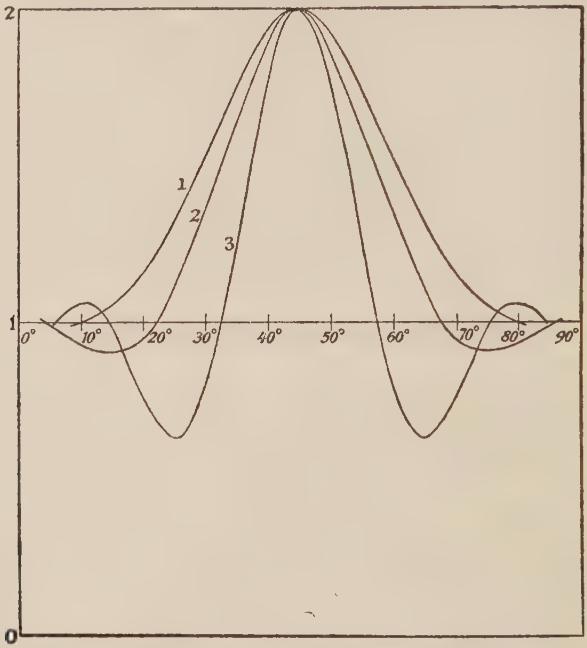

Fig. 1.—Ratio of Quantum Theory Scattering to Classical Scattering, for α-particles of velocity (1) $1 \cdot 92 \times 10^9$ cm./sec. (2) 1×10^9 cm./sec. (3) $0 \cdot 5 \times 10^9$ cm./sec.

§ 2. *The Experimental Method.*—The experimental arrangement was the annular ring method as adapted by Rutherford and Chadwick* for observation of scattering by a gas. Two graphite diaphragms A and B defined the incident beam of α-particles, an annular ring of limits $\frac{1}{2}\phi_1$, $\frac{1}{2}\phi_2$, proceeding from the source S, and a similar pair C and D defined the scattered beam received by the zinc sulphide screen Z (see fig. 2). The discs B and C and the holes A and D were 9 mm. in diameter. The diaphragms were symmetrically placed with respect to the source and screen and their distances were adjusted so that the angles ϕ_1 and ϕ_2 were 40° and 50° respectively. The volume of gas which is effective in scattering particles to Z is an annular ring shown shaded in the figure. The length of the scattering path in the gas was 2·2 mm. and the mean distance of the source (or screen) to the scattering point was 17·9 mm.

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* Rutherford and Chadwick, 'Phil. Mag.,' vol. 4, p. 605 (1927).

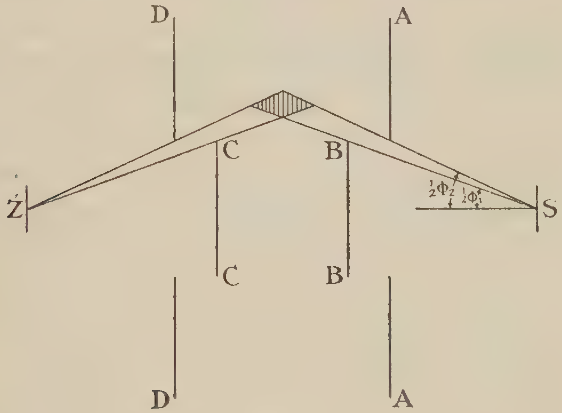

FIG. 2.

If the scattering gas is helium then the number of α-particles arriving per second on unit area of the screen Z should be, on classical theory and for Coulomb forces,

$$\frac{Qntb^2}{16r^2}(\operatorname{cosec}^2\phi_1 - \operatorname{cosec}^2\phi_2),$$

where Q = the number of α-particles emitted per second by the source S; n = the number of atoms of helium per cubic centimetre; t = the scattering path in the gas; r = the mean distance from the source to the scattering region; $b = 2E^2/MV^2$.

Similarly the number of helium nuclei projected by collision of an α-particle so as to reach the screen should be, per unit area per second,

$$\frac{Qntb^2}{16r^2}(\sec^2\phi_2 - \sec^2\phi_1).$$

Under the conditions of the present experiments where $\phi_1 = \frac{1}{2}\pi - \phi_2$, the total number of particles reaching the screen should be

$$\frac{Qntb^2}{8r^2}(\operatorname{cosec}^2\phi_1 - \operatorname{cosec}^2\phi_2).$$

In order to calculate the number of scintillations to be expected on the zinc sulphide screen it is necessary to know not only the geometric conditions of the apparatus but also the efficiency of the screen, Q, the number of α-particles emitted per second by the source, and the quantity b^2, which depends on the fourth power of the velocity of the incident particles. The latter quantity is difficult to estimate directly in those cases when, in order to obtain an incident beam of particles of low velocity, absorbing sheets of mica are placed over the source. All the difficulties can be avoided, however, by comparing the scattering in helium with the scattering in argon under the same conditions. If the pressure of the argon is adjusted to give the same stopping power for the α-particles as in the experiment with helium, then, even if the incident beam of α-particles is heterogeneous, the velocity distribution in the scattering region will be the same in both cases. This calibration with argon is, of course, only valid if the forces between the α-particle and the argon nucleus in these collisions obey Coulomb's law. This was shown to be the case in the experiments of Rutherford and Chadwick for the same angles of scattering and for faster α-particles than are used here.

If the scattering gas is argon the number of α-particles arriving on unit area of the screen per second will be

$$\frac{Qn_1t_1b_1^2}{64r^2}\left[\log\tan\tfrac{1}{4}\phi_2 - \log\tan\tfrac{1}{4}\phi_1 + \cot\tfrac{1}{2}\phi_1 \,.\, \operatorname{cosec}\tfrac{1}{2}\phi_1 - \cot\tfrac{1}{2}\phi_2 \,.\, \operatorname{cosec}\tfrac{1}{2}\phi_2\right],$$

where n_1 = the number of argon atoms per cubic centimetre ; t_1 = the mean value of $t\cos\frac{1}{2}\phi_1$; $b_1 = 36e\,.\,E/MV^2$.

For the geometrical conditions holding in these experiments the ratio of the number of scintillations observed on the screen with helium as scattering gas to those with argon will be 1 to 40, for equal pressures of the gases and for the same incident α-particles.

The details of the apparatus used need little explanation. The source and diaphragms were carried on a brass plate which fitted into slides fixed to the base of a cylindrical brass vessel. The zinc sulphide screen was fixed over a hole in the end-plate of this vessel. The source was enclosed in a small tube the end of which was covered with a thin sheet of mica of stopping power equivalent to 5 mm. of air. This tube was provided with a separate connection to the pump system, to avoid contamination of the scattering chamber. Extraneous scattering was reduced to a negligible amount by careful centring of the diaphragm, source, and screen.

The source of α-particles was a platinum disc of 3·5 mm. diameter coated with polonium. The polonium was obtained on platinum foil by the electrolysis of a solution of radium (D + E + F) and was concentrated on the platinum disc by volatilisation. The amount of polonium was nearly 8 millicuries, *i.e.*, the amount in equilibrium with 8 mg. of radium. The α-particles emitted by polonium have a range in air at 15° C. and 760 mm. pressure of 3·87 cm. Allowing for the absorption in the fixed mica and in the gas the mean range of the fastest incident α-particles used in the experiments was 2·94 cm. By placing sheets of mica in front of the source, in addition to the fixed sheet, the scattering of α-particles of smaller ranges could be examined. In this way experiments were made on the scattering of α-particles of four different ranges, 2·94 cm., 2·04 cm., 1·4 cm., and 1·2 cm. In the latter cases the mean range of the particles was not estimated from the known thickness of the mica sheets placed over the source but deduced from the observations of the scattering of the particles in argon, compared with the scattering of the particles of 2·94 cm. range. With the former procedure it would be necessary to make a difficult and complicated calculation of the correction for the straggling of the particles in their path through the mica and gas.

§ 3. *Results and Discussion.*—Details of the comparison of the scattering of α-particles of average range 2·04 cm. in helium and in argon are given below.

Experiment No. 2.—December 13, 16 and 17. Average range of α = 2·04 cm.

Gas.	Pressure.	Temperature.	Number of scintillations per minute.	Natural effect and contamination.	Corrected number per centimetre pressure.
	cm.	° C.			
Helium	73·0	15·5	16·5	0·2	0·223
	60·0	13·5	13·8	0·2	0·227
Argon	11·16	13·5	36·3	0·2	3·24
	13·0	14·0	48·2	0·2	3·55

therefore

$$\frac{\text{Scattering of helium}}{\text{Scattering in argon}} = \frac{1}{15{\cdot}2}.$$

The details of the other series of experiments were similar. In those with incident α-particles of short range a lower pressure of helium, about 20 cm., was used. The velocity of the α-particle scattered at 45° by collision with a helium nucleus (or of the helium nucleus projected at 45°) is $1/\sqrt{2}$ times that of the incident α-particle. The range of the particles is thus reduced by the collision to about one-third. In order to reduce the absorption of the scattered particles in the gas the pressure of helium was adjusted as low as was sufficient to give a convenient number of particles for counting.

The results of the four series of experiments are collected in the following table :—

Range of α.	E_0/E.	$\frac{\text{Scattering in He}}{\text{Scattering in A}}$.	Ratio to classical scattering.
2·94	1·78	1/24·5	1·63
2·04	2·33	1/15·2	2·66
1·4	3·20	1/18	2·22
1·2	3·68	1/19	2·12

The first column gives the average range of the incident α-particles at the point of scattering, the second the ratio of the energy E_0 of the α-particle of radium C′ (7 cm. range) to the energy E of the particles used in the experiment. As has been stated above, the ranges and energies of the α-particles used in the last three experiments were deduced from the scattering in argon observed in these experiments with that found in the first experiment with α-particles of range 2·94 cm. In making this comparison account had to be taken of the decay of the polonium source. The third column gives the ratio of the scattering observed in helium to that observed for an equal number of atoms of argon ; and the fourth column gives the ratio of the observed scattering in helium to that calculated on the classical theory.

It is clear from the method of experiment that the only source of large error in the final estimation of the scattering by helium lies in the actual observation of the scintillations produced on the zinc sulphide screen, for the only other quantities which enter into the result are the measurements of the pressures of helium and argon. Provided that the scintillations are bright the counting error will be due mainly to the probability fluctuations and can be calculated from the number of scintillations counted in the experiments. The probable error in the final result due to this cause is less than 5 per cent. in each experiment. However, when an α-particle is scattered through 45° by collision with a helium nucleus it loses half its energy. Consequently the scintillations observed in the helium experiments are due to particles of lower energy than those in the argon experiments. This fact is only of importance in the last two experiments in which α-particles of small initial range were used. In these experiments it may be possible that the efficiency of counting was less in the helium observations than in those with argon, though the difference should be small. The result of such a difference in efficiency of counting would clearly be to make the ratios of column 4 of the above table smaller than they ought to be.

The significance of the results given in the above table will be more easily seen by reference to fig. 3, in which the ratio of the observed scattering in helium to the classical scattering is plotted against the value of E_0/E. The observations of the present experiments are shown by circles, while the crosses represent observations made with faster α-particles in the experiments of Rutherford and Chadwick. The dotted line for ordinate unity gives the scattering on classical theory and Coulomb forces, while the dotted line at ordinate 2 (or rather slightly less than 2) represents the scattering which should be observed according to Mott's calculation, again provided that the forces are inverse square. It is clear that the experimental results approach the value of twice the classical scattering as the energy of the incident α-particle decreases, that is, the results approach more and more closely to the quantum theory scattering. A comparison of the amount of scattering observed in the last two experiments shows that in these collisions the forces between the particles vary very little from Coulomb forces. The discrepancy from classical scattering cannot, therefore, be ascribed to a divergence from Coulomb forces and it must be attributed to a failure of the classical theory itself. The experiments thus provide a striking verification of Mott's calculation and of the assumption on which it is based, that it is impossible to distinguish one helium nucleus from another of the same velocity. In other words, the helium nucleus has no spin or vector quantity associated with it, its field of force is perfectly spherical.

Some further remarks may be made about the observations recorded in fig. 3. As the energy of the incident α-particle is increased, *i.e.*, as the distance between the colliding α-particle and helium nucleus is decreased, the observed scattering rises slightly above the scattering calculated on quantum theory and Coulomb forces, then falls to a small fraction of the calculated value, and finally rises very rapidly. The initial rise and fall of the scattering may be due to a true change in the law of force between the particles ; the distances of collision are comparatively large, varying from $7 \cdot 8 \times 10^{-13}$ cm. for the slowest α-particle used to about 4×10^{-13} cm. for the collisions represented by the minimum of the curve. At smaller distances between the particles, for collisions represented by the rapidly rising part of the curve of fig. 3, it seems from these and other observations of Rutherford and Chadwick that the field of force between the particles shows a marked asymmetry. This

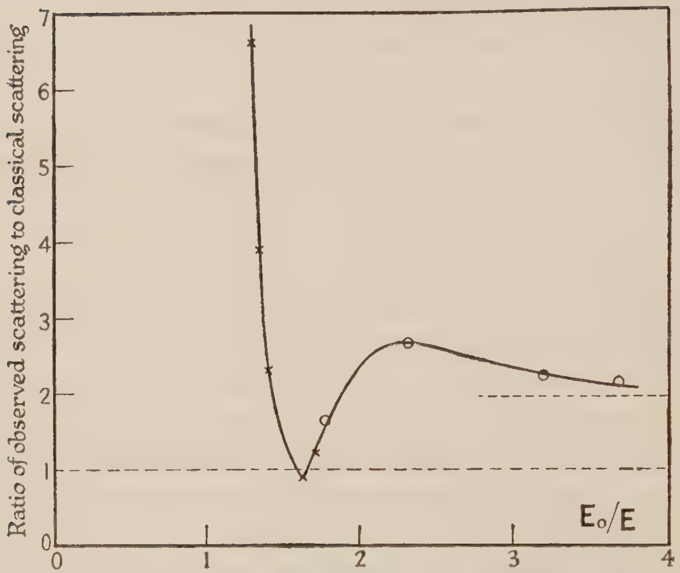

FIG. 3.—Scattering of α-particles in Helium between 40° and 50°.

asymmetry has hitherto been ascribed to the "shape" of the helium nucleus and it has seemed from calculations of Hardmeier* that the effects of polarisation or distortion should be small compared with those observed. Since the present experiments show conclusively that the field of force around the normal α-particle is spherical, the asymmetry shown at small distances of collision can be due to nothing else but a distortion of the structures of the particles. After the collision the structures will presumably regain their original shape very quickly for the time of relaxation of a nucleus must be of the same order as the time of collision, about 10^{-20} second. The scattered α-particles will always be identical with the helium nuclei projected in the same direction for both particles will suffer the same distortion.

My thanks are due to Mr. G. R. Crowe for his help in arranging the experiment and in counting scintillations.

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* Hardmeier, 'Helvetica Phys. Acta,' vol. 1, p. 193 (1928).

A Possible Explanation of the Selective Photoelectric Effect.

By R. H. Fowler, F.R.S.

(Received May 5, 1930.)

§ 1. *Introduction.*—The known facts about the normal and the selective photoelectric effect have recently been assembled and discussed by Campbell.* The theoretical speculations of this paper are the outcome of discussions with him. I take this opportunity of acknowledging my indebtedness to him, for without these discussions I could never have attempted to formulate any such theory.

In the normal photoelectric effect the number of electrons emitted per quantum absorbed increases regularly as the frequency of the light is increased beyond the threshold. (We are throughout this paper only concerned with frequencies of the order of the threshold frequency, usually less than twice as great and never several times greater.) In certain cases, however, when the electric vector of the exciting light lies in the place of incidence, the number of emitted electrons shows a strong fairly narrow maximum superposed on the normal increase, when plotted against the frequency. This is the selective effect. The superposed maximum may be quite near the threshold.

It has only recently become clear under what conditions the selective effect can occur. The evidence reviewed by Campbell seems to be conclusive that no *clean* surface of a metal in bulk shows any selective photoelectric effect, and, indeed, usually no greater emission when the electric vector of the exciting light is nearly normal to the surface than when it is parallel. To this latter there is an important exception. Ives has shown that thin clean layers of an alkali metal on less electropositive supports agree with other clean surfaces in showing no selective effect, but do show a strong preferential emission when the electric vector is normal to the surface. The significance of Ives' work will appear more clearly later. It appears to mean that, while light absorbed by clean thick alkali metal is on the whole absorbed so deep in the metal that when the absorbing electron reaches the surface it has lost all sense of its original direction of projection though it may still retain the greater part of its energy, light absorbed* by the thin backed film is mainly absorbed close to the surface of the support, so that the absorbing electrons can traverse the alkali film without entire loss of their original direction.

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* Campbell, 'Proc. Phys. Soc.,' London (*in press*).

To return to the main point, the essential condition for selective emission appears to be entirely *a condition of the surface*; some version or other of the following process appears to be gone through in every known method of constructing a selective emitter :—On a clean metal surface a layer, a few molecules thick, of a chemical compound is formed between the metal and a more strongly electronegative element—usually oxygen, but hydrogen can function electronegatively for some of the alkalis. A second layer of a strongly electropositive element must then be superposed, during which part of the process the first layer may have to undergo partial reduction. Apparently the essential result is to leave the original metal covered with an electronegative layer from one to a few molecules thick, the whole covered again by a monomolecular electropositive layer. (There is fairly good evidence that the outside layer at its best is strictly monomolecular.) When such surfaces are not matt, so that the relationship of the electric vector to the surface can be defined, the selective effect is not found if the electric vector is parallel to the surface. For further details the reader should consult Campbell (*loc. cit.*). Older information will be found in Campbell and Ritchie "Photoelectric Cells," and some of the most informative work is described by Fleischer and Dember, and quite recently by Fleischer and Teichmann.†

For the convenience of the reader a typical curve of electrons emitted per quantum absorbed by a selective emitter is shown in fig. 1.

Since the condition for the occurrence of the selective effect appears to be entirely a surface one, the conclusion is forced on us that the observed selectivity should be referred to D (W), the transmission coefficient through the surface potential field for an electron incident from within with energy W in its motion normal to the surface. If D (W) were to show a fairly sharp selectivity could one then reasonably explain the observed facts ? In the first place the direction of ejection of a photoelectron from *an atom* is closely correlated to the direction of the electric vector of the exciting light. The

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* [*Added May* 25.—Or rather such light as generates potential photoelectrons. There will necessarily be a potential hill to be passed through at the junction of the two metals by any electron attempting to emerge from the deeper metal so that apart from optical considerations there may be a reason here for a shallow origin for the photoelectrons.]

† Fleischer and Dember, Z. Tech. Phys.,' vol. 3, p. 133 (1926); Fleischer and Teichmann, 'Z. Physik,' vol. 61, p. 227 (1930).

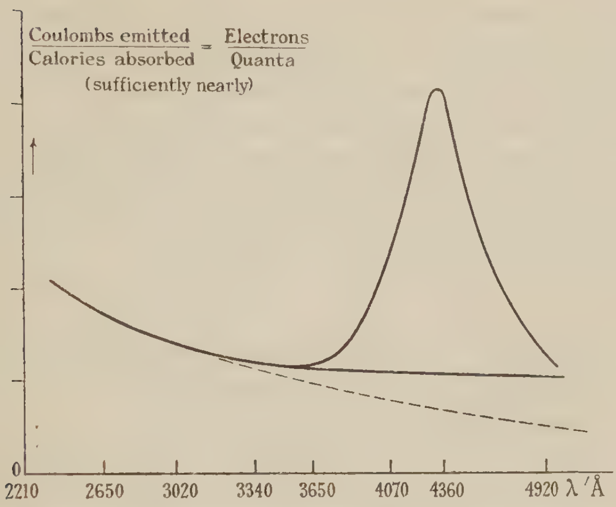

Fig. 1.—Typical curves of Photoelectric Emission. The continuous curves are typical examples shown by Fleischer and Dember (*loc. cit.*) on an arbitrary scale for a potassium cathode in a fairly unselective state and fairly well sensitised with hydrogen. The actual scale of such typical curves may be deduced from Fleischer and Teichmann (*loc. cit.*) who show that at the top of a well-developed peak the ordinate may be about 4×10^{-3} electron per quantum absorbed. The dotted curve represents more nearly the emission typical of an entirely non-selective cathode. The ratio of the peak emission to non-selective emission with a similar threshold may be greater than the value shown in the figure, perhaps as great as 20.

probability of ejection per unit solid angle at an angle θ to the electric vector varies in certain cases like $\cos^2 \theta$. One might expect a somewhat similar variation with θ for the direction of the extra momentum picked up by an electron in a metal. When therefore the electric vector is as nearly as possible normal to the surface,* the electrons that pick up the quanta will go off on the average as nearly as possible in the most favourable direction, and will be more ready than in other cases to emerge without suffering further deflections. When the initial direction of projection is widely removed from the normal to the surface the electron must undergo a considerable number of deflections before it can emerge. Though a number of such deflections by the lattice atoms may only slightly alter the *energy* of the electron owing to the great mass of the atoms, yet there will be a loss of energy on the whole even here, and a serious loss in encounters with electrons. This may well be sufficient apparently to blurr the selectivity out of D (W) for the incident light with its electric vector parallel to the surface, while leaving it in the emissivity curve for the other light. This explanation requires on the average a fair number of nearly elastic deflections for each electron between the moment when it picks up its quantum, and the moment when it falls on the surface with sufficient normal energy to have a chance to emerge. This requirement seems to be quite in keeping with the general nature of the phenomenon, particularly with Ives's experiments on thin alkali films, if they may be interpreted as suggested above.

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* [*Added May* 25.—I am kindly reminded by the Referee of this note that in the phenomenon of metallic reflection as considered in ordinary physical optics the total electric vector of the incident and *reflected* beams is exactly normal to the surface. This of course helps the suggested explanation.]

We appear therefore to be entitled to answer the question of the last paragraph in the affirmative. We proceed to see if D (W) can have selective properties for the type of potential barrier which might be expected to occur for surfaces of the type known to exhibit the selective effect. Any such explanation will obviously make the position of the selective maximum characteristic of the nature of the surface layer. This will be in full agreement with the facts as found by Fleischer and his collaborators for potassium-hydrogen surfaces; they found that the position of the maximum was constant, but its height varied, presumably at least partly with the degree of completeness of formation of the film. We know far too little about the process of light-absorption in the metal and the history of the electron before it emerges to do more than study D (W) itself. We shall find in the next section that D (W) can show just the selectivity that is apparently required.

§ 2. *Selective Features in* D (W).—Once we have dared to admit to ourselves the idea that the selective photoelectric effect may be due to selectivity in D (W), and try to see if any such selectivity theoretically exists, we recognise at once that it does. Such selectivity was found for instance by Fowler and Wilson* in their study of the penetration of α-particles into a model nucleus,

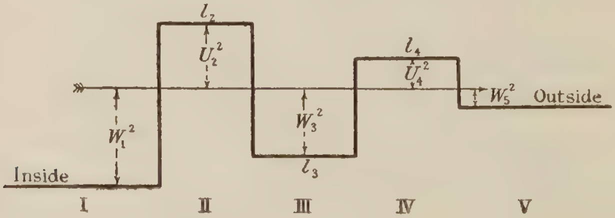

Fig. 2.—The stepped curve represents the assumed potential energy $V(x)$ of an electron near the boundary of the metal. The height of the horizontal line ⟶ represents (with the same zero) the total energy W of the electron.

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* Fowler and Wilson, 'Roy. Soc. Proc.,' A, vol. 124, p. 493 (1929).

and has been examined further by Atkinson, Gamow and others. To exhibit the properties of D (W) as clearly as possible we will repeat the calculations here for the boundary field of fig. 2. The whole ease of the calculation, which is merely complicated by trivialities, lies in the choice of a convenient notation. We therefore use symbols like W_r^2, U_r^2 to denote constant energy differences. These are shown in detail in fig. 2. The proper solutions of the wave equation

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2}+(V-W)\psi=0$$

in the five regions (without time factors), which represent a stream of electrons of energy W falling from the left on the metallic boundary and being partly reflected and partly transmitted there, can be put in the form

$$\begin{aligned}
\psi_1 &= A_1\, e^{i\kappa W_1 x} + A_1'\, e^{-i\kappa W_1 x}, \qquad (\kappa^2 = 8\pi^2 m/h^2),\\
\psi_2 &= A_2\, e^{\kappa U_2 x} + A_2'\, e^{-\kappa U_2 x},\\
\psi_3 &= A_3\, e^{i\kappa W_3 (x-l_2)} + A_3'\, e^{-i\kappa W_3 (x-l_2)},\\
\psi_4 &= A_4\, e^{\kappa U_4 (x-l_2-l_3)} + A_4'\, e^{-\kappa U_4 (x-l_2-l_3)},\\
\psi_5 &= A_5\, e^{i\kappa W_5 (x-l_2-l_3-l_4)}.
\end{aligned}$$

If we write

$$\rho_2 = e^{\kappa U_2 l_2}, \qquad \theta_3 = \kappa W_3 l_3, \qquad \rho_4 = e^{\kappa U_4 l_4},$$

the equations of continuity can be put in the form

$$\left.\begin{aligned} A_1 + A_1' &= A_2 + A_2' \\ iW_1(A_1 - A_1') &= U_2(A_2 - A_2') \end{aligned}\right\}, \tag{1}$$

$$\left.\begin{aligned} \rho_2 A_2 + A_2'/\rho_2 &= A_3 + A_3' \\ U_2(\rho_2 A_2 - A_2'/\rho_2) &= iW_3(A_3 - A_3') \end{aligned}\right\}, \tag{2}$$

$$\left.\begin{aligned} A_3\, e^{i\theta_3} + A_3'\, e^{-i\theta_3} &= A_4 + A_4' \\ iW_3(A_3\, e^{i\theta_3} - A_3'\, e^{-i\theta_3}) &= U_4(A_4 - A_4') \end{aligned}\right\}, \tag{3}$$

$$\left.\begin{aligned} \rho_4 A_4 + A_4'/\rho_4 &= A_5 \\ U_4(\rho_4 A_4 - A_4'/\rho_4) &= iW_5 A_5 \end{aligned}\right\}, \tag{4}$$

The transmission coefficient D (W) depends on $|A_5|^2/|A_1|^2$. On solving equations (4) for A_4 and A_4' in terms of A_5 and equations (3) for A_3 and A_3' in terms of A_4 and A_4' and so expressing them in terms of A_5 we find

$$\left.\begin{aligned}
A_3 &= \tfrac{1}{4}e^{-i\theta_3} A_5\left[\frac{1}{\rho_4}\frac{(U_4+iW_5)(U_4+iW_3)}{iW_3U_4} - \rho_4\frac{(U_4-iW_5)(U_4-iW_3)}{iW_3U_4}\right]\\
A_3' &= \tfrac{1}{4}e^{i\theta_3} A_5\left[-\frac{1}{\rho_4}\frac{(U_4+iW_5)(U_4-iW_3)}{iW_3U_4} + \rho_4\frac{(U_4-iW_5)(U_4+iW_3)}{iW_3U_4}\right]
\end{aligned}\right\}. \tag{5}$$

If, as we shall assume, ρ_4 is fairly large compared with 1, only the second term in each [ ] in (5) need be retained, at least at first. On solving equations (1) and (2) for A_1 (and A_1') in terms of A_3 and A_3' we obtain

$$A_1 = \tfrac{1}{4}A_3\left[\frac{1}{\rho_2}\frac{(U_2+iW_1)(U_2+iW_3)}{iW_1U_2} - \rho_2\frac{(U_2-iW_1)(U_2-iW_3)}{iW_1U_2}\right]$$

$$+\tfrac{1}{4}A_3'\left[\frac{1}{\rho_2}\frac{(U_2+iW_1)(U_2-iW_3)}{iW_1U_2} - \rho_2\frac{(U_2-iW_1)(U_2+iW_3)}{iW_1U_2}\right]. \quad (6)$$

Retaining only the second terms in (5) we find

$$A_1 = \tfrac{1}{16}A_5\left\{\begin{array}{l} \rho_2\rho_4\dfrac{(U_2-iW_1)(U_4-iW_5)}{W_1W_3U_2U_4}\left[\begin{array}{l}(U_2+iW_3)(U_4+iW_3)\,e^{i\theta_3} \\ \qquad -(U_2-iW_3)(U_4-iW_3)\,e^{-i\theta_3}\end{array}\right] \\ -\dfrac{\rho_4}{\rho_2}\dfrac{(U_2+iW_1)(U_4-iW_5)}{W_1W_3U_2U_4}\left[\begin{array}{l}(U_2-iW_3)(U_4+iW_3)\,e^{i\theta_3} \\ \qquad -(U_2+iW_3)(U_4-iW_3)\,e^{-i\theta_3}\end{array}\right]\end{array}\right\}. \quad (7)$$

If we had retained the terms in $1/\rho_4$ there would also have been terms in ρ_2/ρ_4 and $1/\rho_2\rho_4$ in (7).

Now in general ρ_2 and ρ_4 are both fairly large, so that the order of A_1/A_5 is in general $\rho_2\rho_4$. But if by exception

$$(U_2-iW_3)(U_4-iW_3)\,e^{-i\theta_3} = (U_2+iW_3)(U_4+iW_3)\,e^{i\theta_3}, \quad (8\text{A})$$

the order of A_1/A_5 falls to ρ_4/ρ_2 according to (7) or rather to ρ_4/ρ_2 or ρ_2/ρ_4, whichever is the greater, if the other terms in (5) are retained. But equation (8A) is exactly the equation determining the characteristic energies for a hole of the form of region III in fig. 2, when the walls of regions II and IV are extended to infinity. Such a hole is shown in fig. 3.

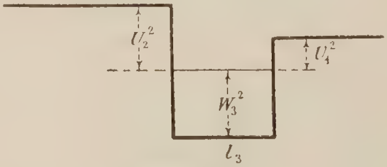

FIG. 3.

It is unnecessary to give the verification that the characteristics satisfy (8A) or

$$e^{2i\kappa W_3 l_3} = \frac{(U_2-iW_3)(U_4-iW_3)}{(U_2+iW_3)(U_4+iW_4)}, \quad (8\text{B})$$

i.e.,

$$\kappa W_3 l_3 = n\pi + \varepsilon. \quad (9)$$

The exact formula for the transmission coefficient is, in the present notation in which U's and W's are *square roots* of energies,

$$\mathrm{D}\,(\mathrm{W}) = \frac{\mathrm{W}_5\,|\,\mathrm{A}_5\,|^2}{\mathrm{W}_1\,|\,\mathrm{A}_1\,|^2}. \tag{10}$$

Since the necessary range of variation in D (W) has obviously been achieved, the factors ρ_2 and ρ_4 being easily as large as 10 or even 100, it only remains to examine whether the necessary hole in the potential barrier is of reasonable dimensions. Equation (9) requires approximately

$$\mathrm{W}_3{}^2 = \frac{n^2\pi^2}{k^2 l_3{}^2} = n^2\,\frac{h^2}{8ml_3{}^2}.$$

Let us suppose that the width of the dip is of the order of $3 \times 10^{-8} \rightarrow 10^{-7}$ cm., say $l_3{}^2 = 10^{-15} \rightarrow 10^{-14}$ cm.^{2}. Then the characteristic energies are given by

$$\mathrm{W}_3{}^2 = 6{\cdot}0 \left\{\begin{matrix}10^{-13}\\ 10^{-12}\end{matrix}\right\} n^2 \text{ ergs}$$

$$= \left\{\begin{matrix}0{\cdot}37\\ 3{\cdot}7\end{matrix}\right\} n^2 \text{ electron volts.}$$

Within these limits it is entirely possible for there to be just one favourable range of values of D (W) and no more for values of W between the threshold and the top of either potential hump, above which height there can be no more characteristics. The virtue of a good red-sensitive emitter lies in combining a sufficiently low threshold energy or frequency, which can only be achieved by a surface double layer and therefore at the expense of a potential hump, with a hollow in that hump forming an approximate characteristic energy of its own which lies only just above the threshold.

§ 3. *Nature of the Surface Layer.* -The potential in the surface layer of the last section is, of course, completely conventionalised. Its essential feature, if the theory is right, is that it consists of *two* hills separated by a rather deep valley. Chemically we know that the surface is constructed of electropositive-electronegative-electropositive materials, the last monomolecular. With the effect of this outside layer we are well acquainted in thermionic emission. It always brings down the potential energy sharply from a hill to a lower level outside. We are thus confident enough that we must have the state of things shown in fig. 4. As to why the valley forms there is as yet little to say. One cannot claim to account for it theoretically, but one can only claim that it is quite reasonable that it should be there.

One further remark in conclusion. The reference of the selectivity to D (W) here given accounts, as we said before, most satisfactorily for the fixed position of the selective maximum for a given type of surface layer. But it may well account also for the variability of the height of the peak even if the layers are generally complete and not patchy. For the *position* of the maximum is fixed only by the nature of the valley, here by l_3, W_3, U_2 and U_4, while the *height* of the peak, that is $(D(W))_{\text{max.}}/(D(W))_{\text{normal}}$ is controlled mainly by ρ_4^4 or ρ_2^4, whichever is the smaller. This can vary with the width of the hills (*i.e.*, the width of the layers) without any effect on the valley (*i.e.*, on the position of the maximum).

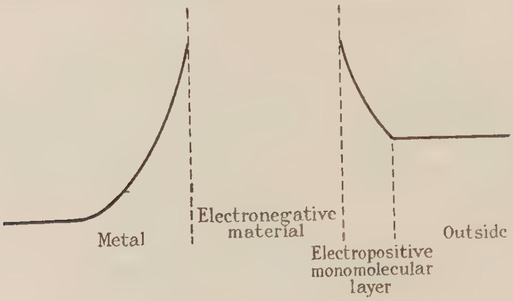
Metal
Electronegative material
Electropositive monomolecular layer
Outside

FIG. 4.

The Ultra-Violet Transmission-Band of Metallic Silver, as Affected by Temperature.

By Lord RAYLEIGH, For. Sec. R.S.

(Received May 8, 1930.)

[PLATE 1.]

The reflecting power of metals in general falls off towards the blue end of the spectrum. This may readily be verified in a qualitative manner by placing a candle between two reflecting surfaces and observing the train of images. These, in all cases that I have tried, become redder as we proceed along the train.*

Silver, however, differs from the other white metals, in that there is a fairly sharp minimum of reflexion in the near ultra-violet. This was first observed by Stokes.†

Cornu‡ found that thin films of the metal are relatively transparent near the region of poor reflexion. The most complete investigation of the reflexion at different wave-lengths is by Minor,§ who examined the elliptical polarisation by reflexion, and thus determined the refractive index and absorption coefficient. The reflecting power depends on both these constants, though the latter has the more important effect in determining the minimum reflexion. Minor found that the minimum reflexion was not at quite the same position in the spectrum as the maximum transmission.

The selective transmission is highly localised in the spectrum, as compared with most other selectively transmitting media which are available to experimenters, and has found important applications in astrophysics. It will also, doubtless, prove to be of considerable theoretical importance when we know more of the mechanism of metallic absorption.

The object of this note is to examine in a preliminary and qualitative way the effect of temperature on the position and breadth of the transmission band.

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* According to the measurements of Hagen and Rubens the magnesium-aluminium alloy called magnalium is sensibly uniform in reflecting power for all parts of the visual spectrum. I find, however, that magnesium alone or aluminium alone behaves as above, giving successive images which become conspicuously redder.

† 'Phil. Trans.,' vol. 162, p. 599 (1862).

‡ 'Ann. Sci. École Norm. Sup.,' vol. 9, p. 21 (1880).

§ 'Ann. Physik,' vol. 10, p. 617 (1903).

I undertook this in the hope that some striking effect might appear (*cf.* superconductivity). This has not been the case within the temperature range used, but the result is definite as far as it goes, and probably not without significance.

The silver used is in the form of commercial silver leaf, which is of suitable thickness though full of holes. To select a good piece a leaf was floated on water, and a piece of perforated zinc with 3 mm. holes was brought up from below. In this way the silver leaf covered the apertures of the zinc, and adhered after drying. An aperture was selected over which the silver appeared free from holes, using a magnifier with a light behind. The zinc was then trimmed to a convenient small size, with this selected aperture in the middle.

To control the temperature of the small silver light filter, it was placed in a covered cavity in the end of a 2·5 cm. vertical copper rod. A horizontal hole about 4 mm. diameter allowed the light to pass. The source was the continuous spectrum of hydrogen from a suitable silica discharge tube. The transmitted light was photographed with a small quartz spectrograph. A thermometer inserted in an independent hole in the copper near the silver indicated the temperature sufficiently well. The bottom end of the rod could be heated in a flame or cooled in liquid air.

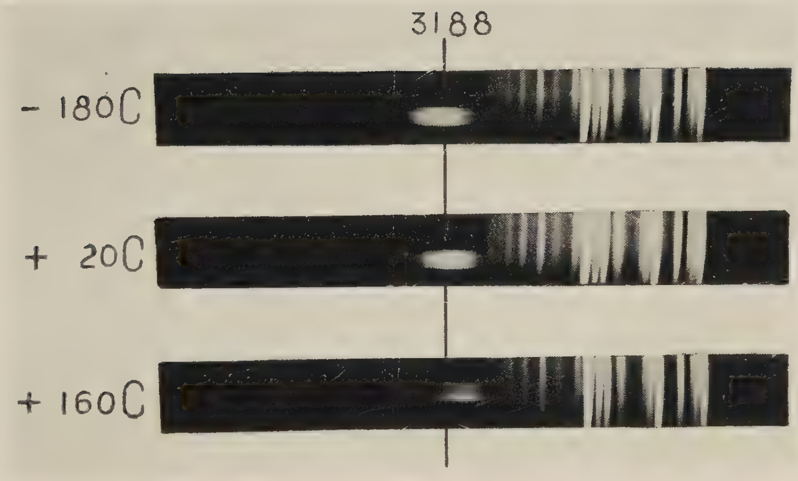
It was then found that a rise of temperature caused a definite shift of the transmission maximum to the red.

When the copper rod was cooled in liquid air, the shift was to the side of short waves, but was less conspicuous than in the previous case.

When cooling in liquid air it was necessary to prevent the circulation of air near the cooled metal, with consequent deposition of hoar-frost. The top end of the copper rod was wrapped in insulating material, and the horizontal tunnel was prolonged externally by glass tubes, each 4 cm. long and 1 cm. diameter, open at the ends.

The *breadth* of the transmission maximum was not conspicuously affected so far as could be judged. The *position* of the maximum was estimated as below, using a helium comparison spectrum and a wave-length scale :—

Temperature. C.	Wave-length. A.
−180	3180
+ 20	3200
+107	3240
+160	3250
+254	3300


3188
- 180C
+ 20C
+ 160C

These measurements are not very accurate, owing to the diffuse character of the band. There is, however, no doubt at all of the general result, a shift of the transmission maximum to the red with rise of temperature. The photographs reproduced in Plate 1 will enable the reader to satisfy himself of this. The transmission band is to be compared with the helium line 3188, which owing to the fact that a glass discharge tube was used is the last helium line in the spectrum. It will be seen that the transmission band, which initially lies almost symmetrically to this line, is displaced by heating so as to be almost wholly on the red side of it.

Some Simultaneous Observations on Downcoming Wireless Waves.

By E. V. Appleton, F.R.S., and J. A. Ratcliffe, M.A.

(Received March 11, 1930.)

(1) *Introduction.*

The present communication deals with a series of observations on downcoming wireless waves made simultaneously at three receiving stations, situated at different distances from the wireless sending station. The original series of experiments, of which this series is a development,* was carried out chiefly over a distance of transmission of about 80 miles. This distance was chosen because, for the 400-metre waves used, the intensity of downcoming waves, at night, is an appreciable fraction of the ground wave intensity, so that conditions are specially favourable for the detailed study of the various characteristics of downcoming waves by methods in which the ground waves are used as reference waves. There seemed, however, many reasons for making observations at shorter distances if downcoming waves could be satisfactorily detected there, while there was more to justify the simultaneous use of several receiving stations than the mere confirmations given by duplicate measurements. For example, it was realised that, according to the ionic refraction theory of the atmospheric deviation of wireless waves, the minimum electronic density necessary to bend back the waves increases as the angle of incidence is decreased, so that measurements of the equivalent height of the ionised layer at different distances might be expected to yield information relating to the gradient of ionisation in the layer, a subject on which precise information is entirely lacking. Further, the results of single station working between Teddington and Peterborough had suggested that, during the few hours before sunrise, the region of ionisation, which normally reflects 400-metre waves, often becomes penetrable for waves of a certain angle of incidence, there being, on such occasions, discontinuous changes in the results of a series of measurements of the equivalent path of the atmospheric rays. It appeared, therefore, of interest to test whether such phenomena were simultaneously observed for atmospheric waves of different angles of incidence such as would ultimately be received as downcoming waves at different distances. Finally, although estimates have been made of the reflection coefficient of the ionised region for particular distances of transmission, there were no data relating to the variation of the atmospheric wave intensity with angle of incidence, such as could only be obtained from simultaneous observations on the radiation from the same transmitter. It is obvious that this last-mentioned subject is of more than scientific interest for it has an important bearing on the practical problem of the prediction of the service areas of broadcasting stations at night.

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* 'Roy. Soc. Proc.,' A, vol. 113, p. 450 (1926), and vol. 126, p. 542 (1930).

The account of these investigations, given below, is divided into two sections, numbered (2) and (3), dealing with the measurements of equivalent height and the measurements of reflection coefficient respectively. These are followed by a general discussion of results (Section 4).

(2) *Simultaneous Equivalent Height Measurements.*

(*a*) *Experimental Arrangements.*—The measurements of the equivalent height of the ionised regions responsible for deviating wireless waves were carried out using the frequency-change method. Details of this method and an account of results obtained by it at a single receiving station have been given in previous papers.*

For the simultaneous observations it would have been desirable to have all the receiving stations, together with the transmitting station, in a straight line. A certain amount of variation from this ideal was, however, necessitated by the small number of available sites which could be conveniently reached by the observing personnel. In view of the desirability of maintaining continuity with the earlier series of observations the Peterborough Radio Research Station was naturally chosen as the most distant receiving station. This station is situated at a distance of 131 km. from the National Physical Laboratory Transmitting Station (5HW) at Teddington, which was used for the greater part of the series of observations. A second receiving station was installed at the Radio Research Board hut at the Cambridge University O.T.C. Rifle Range, Cambridge, which is 91 km. from the Teddington transmitter, while a third station was installed at King's College, London, which is only 18 km. from Teddington. For simultaneous measurements of the equivalent height by the frequency-change method at three receiving stations eight workers in all were required, namely, two to work the transmitter and two to make the necessary observations at each receiving station. The special transmissions required were carried out by E. L. Hatcher and A. C. Haxton of the National Physical Laboratory Wireless Division; the observations at the Peterborough Station were made by A. L. Green and W. C. Brown, those at Cambridge by J. A. Ratcliffe and W. F. B. Shaw, while those at King's College, London, were made by E. V. Appleton and R. D. Gander. Each receiving station was fitted with a high-frequency amplifier sufficiently unselective to give a fairly constant response over the frequency range (of the order of 20,000 cycles per second) used. The output from the high-frequency amplifier was fed into a rectifier system consisting of either a crystal detector or a balanced valve rectifier. The rectified current was recorded photographically by means of a Cambridge Einthoven galvanometer and camera. The aerial system used at King's College, London, was to some extent peculiar, due to the unsatisfactory nature of the site. It consisted of a vertical wire, hung midway between two buildings, with a small horizontal portion suspended about 10 feet above one of the buildings. At the other two receiving stations, since each site consisted of an open field, it was possible to use large loop aerials the directive properties of which were extremely useful in cutting out interference.

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* 'Roy. Soc. Proc.,' A, vol. 109, p. 621 (1925); vol. 113, p. 450 (1926); vol. 115, p. 291 (1927); vol. 126, p. 542 (1930).

The programme of each morning's run was arranged beforehand and usually consisted of a series of 50-second tests sent, at equal intervals, six (or eight or twelve) times during each hour. Each test consisted of ten frequency changes each lasting 3 seconds, separated by intervals of 2 seconds. A scheme of morse signals sent out by the transmitter was arranged to indicate the timing of the frequency change. That this scheme worked satisfactorily is largely due to the accurate way in which the transmissions were sent out from the National Physical Laboratory.

(*b*) *Experimental Results.*—The data relating to simultaneous equivalent height measurements to be reviewed were obtained on 16 early morning runs, during the majority of which all three receiving stations were functioning. In other cases two receiving stations only were working. In order to vary the distance of transmission as much as possible, a few observations were made on transmissions from the Bournemouth B.B.C. station as well as on those from the National Physical Laboratory. It was considered desirable to keep the wave-lengths used within the range of medium wave-lengths (200 to 500 metres) so that the results would be comparable with those used in the single receiving station working. The wave-lengths used were therefore 400 (or 410) and 212 metres for the National Physical Laboratory transmissions and 330 metres for the Bournemouth transmission. The wave-length of 400 metres was chosen because it was when using this wave-length, working between Teddington and Peterborough, that the great equivalent heights had been found. The wave-length of 212 metres was chosen because certain writers have supposed that, since this wave-length corresponds in frequency to the gyro-frequency of free electrons in a magnetic field equal to that of the earth, anomalous results might be obtained using this wave-length. The limitation of the wave-length of the Bournemouth transmitter to 330 metres was imposed by the nature of the particular transmitter circuit used there.

As it is obviously impossible to give the details of all the results obtained at all the receiving stations for the whole series of tests, a selection of the data has been made, which is given below, together with notes as to whether the phenomena experienced were typical or exceptional. In each case, where necessary, the applicability of the hypothesis of the existence of two deflecting regions (Lower Region (E) and Upper Region (F)*) is discussed.

Test No. 48. February 11, 1928.—5.40 to 7.53 a.m. G.M.T. Teddington Transmitter. Wave-lengths used 400 and 410 metres. Sunrise 7.23 a.m. G.M.T.

This was the first occasion on which the King's College observations were made. Unmistakable " fringes " were obtained indicating that downcoming waves of small but appreciable intensity were being received at a place only 18 km. from the sending station. Such atmospheric deviation corresponds to " reflection " at almost vertical incidence. It was, however, found that, due to the relatively small intensity of the downcoming waves, the numbers of signal maxima on many of the London (King's College) records could not be counted. For the complete description of the sequence of events we must refer to the Peterborough series of observations in this case. Here it was found that rays from F region were received at first, the maximum equivalent height of 268 km. being observed at 6.0 a.m. (*i.e.*, 83 minutes before sunrise). The jump down from F region to E region took place about 7.0 a.m. (*i.e.*, 23 minutes before sunrise), after which E region fell from 127 km. recorded at 7.10 to 94 km., recorded at 7.40 a.m.

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* 'Roy. Soc. Proc.,' A, vol. 126, p. 542 (1930).

The London and Cambridge series of observations were, however, complete enough to enable us to compare a few simultaneous readings. For example, at 5.50 a.m. all three stations measured great heights as follows: London 272 km., Cambridge 242 km., and Peterborough 252 km. At 7.10 a.m., just after the discontinuity had occurred, as indicated by the Peterborough observations, the height of the newly formed E region was measured as 125 km. by London, 125 km. by Cambridge and 127 km. by Peterborough.

The results of this test therefore suggested very definitely that the equivalent heights measured at the three stations were not widely different in spite of the differences in transmission distance.

Test No. 49. February 25, 1928.—4.10 a.m. to 7.40 a.m. G.M.T. Sunrise 6.58 a.m. G.M.T. Teddington Transmitter. Mean wave-length 410 metres.

The results of this run were quite normal so far as the Peterborough measurements were concerned, the equivalent height rising slowly on the average until about 25 minutes before dawn when a rapid and continuous reduction took place, an average equivalent height of 86 km. being finally recorded. Similar results were obtained at both Cambridge and London except that at these stations there were particular intervals when greater equivalent heights were recorded. For example at 5.15 London registered 240 km. and Cambridge 236 km., while at 6.30 the corresponding heights were 185 km. and 187 km. respectively. The test therefore showed that on this occasion the observations at stations nearer the transmitter yielded evidence of singly reflected rays from F region (F_1 rays) although no such evidence was obtained at the more distant station. Moreover, it was noted that there were more occasions on which such rays were recorded at London than at Cambridge, which is what one would expect according to the ionic refraction theory of atmospheric deflection, for, with a given intensity of ionisation, there is a greater probability of penetration for normal than for oblique incidence on the layer. The agreement in the measurements of the equivalent heights at the three stations was quite good throughout the night for rays reflected at both E and F regions, but after sunrise, when the lowest values were recorded, there seemed to be differences, the average value at London being 100 km., that at Cambridge 88 km. while that at Peterborough was 86 km.

Test No. 50. March 10, 1928.—Teddington Transmission (400 metres) received simultaneously at Peterborough, Cambridge and London. 4.00 a.m. to 7.20 a.m., sunrise 6.30 a.m.

The equivalent height of reflection as determined at the three stations, at intervals of 10 minutes, and more frequently during the sunrise period, is shown as a function of the time in fig. 1. The figure includes some determinations made on the assumption of double reflection from F region which take the form, in the photographic records, of very numerous fringes. These determinations are shown as crosses in the figure, and it will be seen that they agree very well with the direct determinations. From this figure it will be seen that all three stations recorded deviation from the lower (E) region at a height of 120 km. in the early part of the test between 4.00 and 4.20. It appears that by about 4.20 a.m. recombination of ions in the upper atmosphere had progressed so far that the ionic density of the E region became too small to return the waves at this height. After this time deviation took place at an equivalent height of about 180 km. (F region) until 6.00 a.m. On the next record, taken at 6.07½ a.m., all three stations recorded, once more, a lower equivalent height of 120 km. After this time the equivalent height decreased slowly to about 95 km. and the intensity of the downcoming wave decreased simultaneously. The London station was unable to continue observations after 6.40 because of the extreme weakness of the downcoming ray compared with the direct ray. At 7.35½ (the last observation made) the Peterborough station recorded a larger number of fringes, which must probably be interpreted as being due to a temporary return to deviation at the upper (F) region, at a height of 160 km.

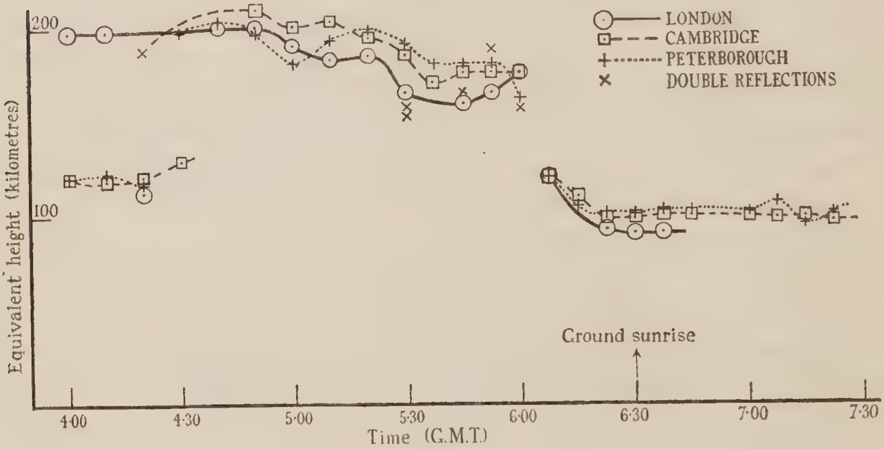

Fig. 1.

From this series of observations there is good reason to believe that the change upwards from deviation at the E region to deviation at the F region is discontinuous. The heights as measured during the first few frequency changes are given in Table I. We see that, in the first two determinations, London registered the F region while Cambridge and Peterborough registered the E region. This is just what we should expect on the hypothesis of two distinct deviating regions if we remember that the E region is more penetrable for the rays which fall on it with smaller angle of incidence. At 4.20 all stations recorded deviation from the E region, and at 4.50 all recorded the F region. The fact that both regions are recorded simultaneously during this period, when we know that recombination has almost proceeded so far that the E region is penetrable, and the fact that, in the case of reception at London, we get a momentary "jump back" to the reflection at the E region, lend strong support to the hypothesis that the change from the E to the F region is discontinuous.

Table I.

	Time :	4.00.	4.10.	4.20.	4.30.	4.40.	4.50.
		(Effective height in kilometres.)					
London .... (distance 18 km.)	E region	—	—	113	—	—	—
	F region	198	197	—	—	200	200
Cambridge .... (distance 91 km.)	E region	119	117	120	—	130	—
	F region	—	—	188	—	—	208
Peterborough .... (distance 131 km.)	E region	120	119	115	—	—	—
	F region	—	—	—	197	201	197

Once reflection from the F region is definitely established, we find good agreement between the heights as measured at the three stations. There seems to be a tendency, however, as the dawn approaches, for the heights, as measured at the three stations, to arrange themselves so that the greater heights are recorded by the more distant stations. From the series of records obtained near 6.00 a.m. there is no reason for supposing that the downwards change from deviation by F region to deviation by the E region is discontinuous, though we believe it to be so, because of the evidence obtained on other occasions. After 6.20, when the reflection from E region is definitely established at all the stations, we again observe the tendency for the measured equivalent height to be greater at the more distant stations.

At 7.30 and 7.37½ the Peterborough station recorded a large number of fringes corresponding to an equivalent height of about 160 km., which presumably indicates a momentary return to reflection by the F region. It is, however, possible that the large numbers of fringes recorded here are due to a doubly reflected ray (E_2) from the E region, but on this assumption the calculated height of the E region is found to differ considerably from that calculated from the small number of fringes (due to ray E_1), and the agreement is not nearly so good as that obtained for the assumption of double reflection from the F region during the earlier portion of the morning, as shown by the crosses in fig. 1. We therefore consider that these large numbers of fringes represent a return to reflection by the F region, due to a momentary decrease in the ionisation of the E region.

We now turn to the question of the differences between the effective heights as recorded at the three stations. We notice that just before the jump up from E to F region, good agreement is obtained between the three measured heights (period 4.00 to 4.20) and just after the jump down (at 6.07½) all three stations record the same height. As we have already pointed out, the same agreement is not apparent during the period 5.20 to 6.00 when reflection from the F region is well established, nor during the period 6.20 to 7.20 when reflection from the E region is well established. During both these periods the more distant the station the greater is the height which it records. It would be possible to explain a discrepancy between the heights recorded, by supposing that the frequency change had not been measured correctly at the transmitting station, and this would be the natural assumption to make were it not for the fact that the agreement between the measured heights is so good during the period 4.00 to 4.20, and at 6.07½. Because of this good agreement we are led to suppose that the frequency change was accurately measured at the transmitting station, and that the value assumed in our calculations is the correct one. We must, therefore, attribute the discrepancy in the measured heights to some cause in the atmosphere itself. The question of how the atmosphere might give rise to an effect of this kind is postponed to the discussion in Section (4) (p. 153).

Test No. 53. April 13, 1928.—3.40 a.m. to 6.30 a.m.; Teddington Transmission received at Ditton Park (Datchet) and Peterborough. Sunrise 5.9 a.m. Wave-length 410 metres.

As it was found at King's College that the small ratio of downcoming wave intensity to ground wave intensity sometimes caused the fringes to be so small as to preclude accurate counting, attempts were made there to use a loop antenna, turned almost to the position for minimum ground ray signal so as to increase this ratio. Due, no doubt, to the nature of the site it was found that the usual minimum position could not be obtained with such a loop antenna, and it was decided to move the necessary apparatus from the station to a more open site at the Radio Research Station, Ditton Park, Datchet, situated 18 km. from Teddington. This particular test is one of a series made at the latter station. A large outdoor loop antenna was used which was adjusted so as to be almost in the position for receiving minimum ground ray signal, and it was found that, as a result, the fringe amplitude was much increased.

On this occasion both E and F regions were observable, the equivalent height measurements being as shown in the Table II below.

Table II.

	Time a.m. :	3.40.	3.50.	4.0.	4.10.	4.20.	4.30.	4.37.	4.45.
		(Height in kilometres.)							
Ditton Park	F region	244	244	244	264	308	220	198	186
	E region	—	—	—	—	—	—	—	—
Peterborough	F region	233	243	223	245	240	210	200	—
	E region	—	123	—	—	—	—	118	117

	Time a.m. :	4.52.	5.0.	5.7.	5.15.	5.22.	5.30.	5.37.
		(Height in kilometres.)						
Ditton Park	F region	—	186	—	—	—	—	—
	E region	122	115	110	114	118	107	110
Peterborough	F region	—	—	—	—	—	—	—
	E region	117	114	108	109	103	103	101

There are various interesting features in these results. In the first place it will be seen that E region was observed at Peterborough to a greater extent than at Ditton Park. For example at 3.50 a.m. reflection from a height of 123 km. was found at Peterborough but not at Ditton Park. Also the change-over from F region to E region took place earlier at the former station than at the latter. The results also show that although there is a fair agreement between the heights measured at the two stations as a whole, there are two sets of observations which show a marked discrepancy. These are the readings taken at 4.10 and 4.20 which show that the equivalent heights measured at Ditton Park are quite definitely greater than those observed at Peterborough. The variation of equivalent height with time at Peterborough was of the type experienced on many occasions but that observed at Ditton Park was unusual. It is therefore exhibited in fig. 2.

The Ditton Park series of observations show the change-over from F region to E region in a very interesting manner and exhibit clearly the discontinuity. To illustrate this, parts of the photographic records obtained between 4.45 a.m. and 5.7 a.m. are reproduced in fig. 3 (*a*) to (*d*). These records correspond to points on fig. 2. The wave-length change was in each case 10 metres. In fig. 3 (*a*), which was taken at 4.45 a.m., there are 21·5 fringes corresponding to an equivalent path difference of 345 km. and thus reflection from F region. In the first half of the frequency change it will be seen that there are signs of fringes approximately half as frequent. Fig. 3 (*b*) is a reproduction of a record taken at 4.52 a.m. when E region was sufficiently developed to reflect, and 12·8 fringes were obtained, corresponding to an equivalent path difference of 215 km. At 5.0 a.m., however, there was a partial return to F region for, in fig. 3 (*c*), which shows a record taken at that time, 21 fringes can be counted as well as a smaller number which is approximately 12. (Another frequency change on the same record showed the smaller number more fully developed and there it is found to be 12·2.) Fig. 3 (*d*), taken at 5.7 a.m. shows the final establishment of E region, there being 11·5

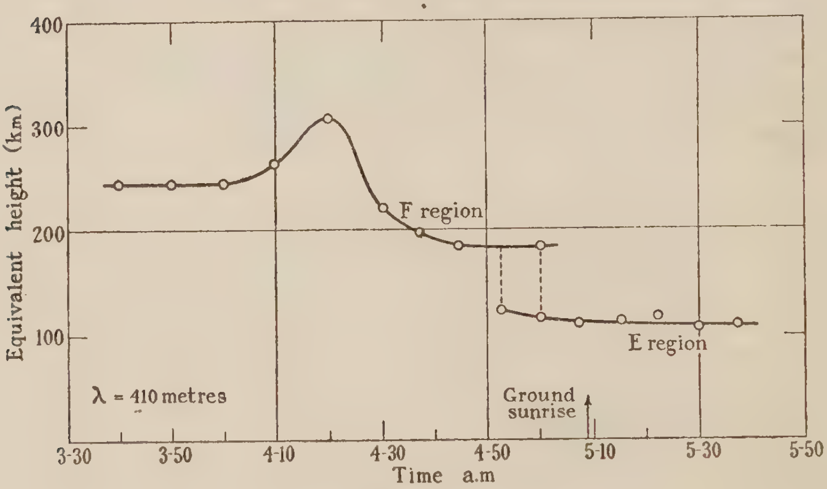

Fig. 2.

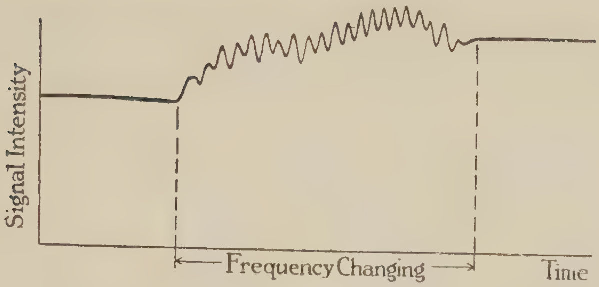

FIG. 3*a*.

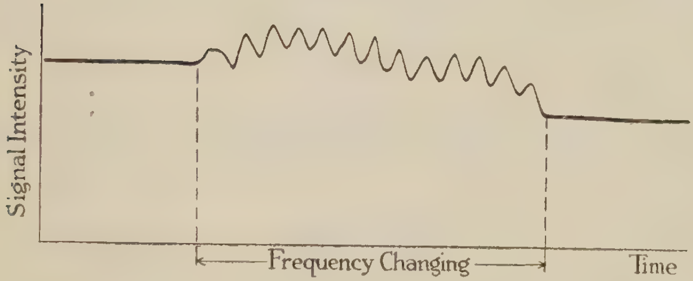

FIG. 3*b*.

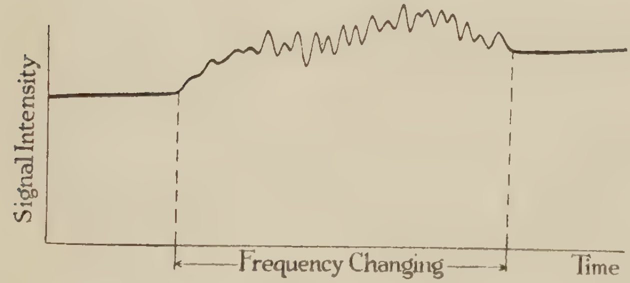

FIG. 3*c*.

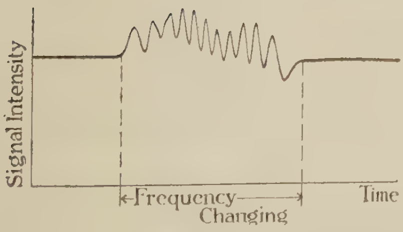

FIG. 3*d*.

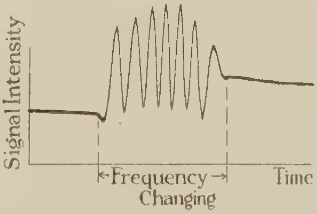

FIG. 3*e*.

fringes. All the other records after this showed the same or a smaller number, though in the ones immediately following there were also signs of 20 to 21.

The partial return to F region at 5 a.m. seems to exclude definitely the possible supposition that the layer had fallen continuously from 186 km. to 122 km. during the period from 4.45 a.m. to 4.52 a.m., and that intermediate values had been missed because of the discontinuous method by which the observations have been made.

In fig. 3 (*e*) is exhibited a record taken at Peterborough for comparison with fig. 3 (*d*). It was taken at exactly the same time and is of interest as showing the smaller number of fringes, because of the smaller equivalent path difference at the greater distance and also the marked difference in the relative strength of downcoming wave intensity compared with ground wave intensity. In estimating this relative intensity we must also remember that at Ditton Park the ground wave was eliminated to a great extent by the use of the loop in the minimum position.

Test No. 56. May 19, 1928.—3 a.m. to 7 a.m.; Teddington transmitter, received at London, Cambridge and Peterborough. Wave-length 212 metres. Sunrise 4.9 a.m.

This test may be considered typical of the series of runs on 212 metres. The series as a whole served to show fairly definitely that the 212-metre waves behaved very similarly to the 400-metre waves, apart from such differences as might have been predicted. For example, the fringe amplitudes at London were much larger on 212 metres than on 400 metres, being, in fact, comparable with those obtained at Ditton Park when a loop antenna, turned nearly to the minimum position, was used. Equivalent heights of E region were found to be about the same as with 400-metre waves, while the same lack of evidence of marked variation of equivalent height with angle of incidence was noted. For F region, however, it was found that although good agreement between the equivalent heights measured at the three stations was usual, these heights were, on the average, somewhat greater than those obtained with 400-metre waves at about the same time of the morning.

In the test under discussion there are many gaps in the Peterborough series of observations due to atmospheric interference, but a fairly complete comparison of the London and Cambridge measurements can be made. These are exhibited in Table III.

The heights as measured at the two stations are seen to agree fairly well. The values of the height of F region at the time when E region first begins to reflect are higher than is usually the case with 400 metres. Moreover, there is no sign of the usual fall in the height of F region during the period just before E region begins to reflect. An interesting feature of the results is that, at both stations, numbers of fringes corresponding to a height which is approxi-

Table III.—Equivalent Height Measurements, May 19, 1928.

	Time a.m. :	3.15.	3.22.	3.30.	3.37.	3.45.	3.52.	4.0.	4.10.	4.20.
		(Height in kilometres.)								
London (King's College)	F region	245	256	260	261	289	—	—	—	—
	E region	—	—	—	—	121	(217) 110	(234) 116	110	110
Cambridge	F region	—	—	255	270	282	270	—	—	—
	E region	—	—	—	109	115	119	113	(222) 111	113

	Time a.m. :	4.30.	4.40.	4.50.	5.0.	5.10.	5.20.	5.30.	5.40.	5.50.
		(Height in kilometres.)								
London (King's College)	F region	—	—	—	—	—	—	—	—	—
	E region	110	121	110	105	99	99	99	99	99
Cambridge	F region	—	—	—	—	—	—	—	—	—
	E region	120	115	109	103	97	96	97	99	99

mately twice that of E region were found. The equivalent heights corresponding to these numbers are given in brackets in the E region column, because they are considered as being cases of double reflection from that region. In this connection it may be noted that on many occasions we have found examples of double reflection by E region just after it has formed in sufficient density to reflect in the early morning.

Another interesting feature of the series is that after the formation of E region there seemed at all three stations evidence of two downcoming rays with a slight difference of equivalent path. For example, on certain records some frequency changes show 5·5 fringes, while others show as many as 7·0, while on others both are present. It is not considered possible for the frequency changes at the transmitter to have varied sufficiently in value to cause these differences, and there therefore does seem to be real evidence of two downcoming rays with slightly different equivalent paths. The possibility of this has been previously suggested.* For calculating the equivalent heights shown in Table III mean values of numbers of fringes have been taken.

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* 'Roy. Soc. Proc.,' A, vol. 115, p. 315 (1927).

Examples of the type of interference variations experienced simultaneously at the three stations (London, Cambridge and Peterborough) during this test are shown in figs. 4, (*a*), (*b*) and (*c*). The time at which the records were obtained was 4.10 a.m.

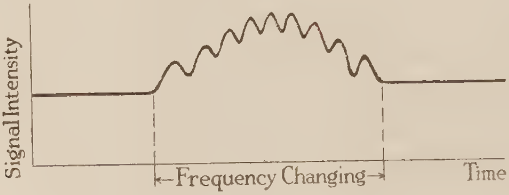

Fig. 4*a*.

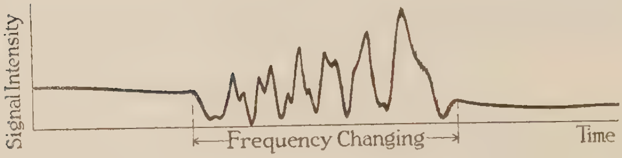

Fig. 4*b*.

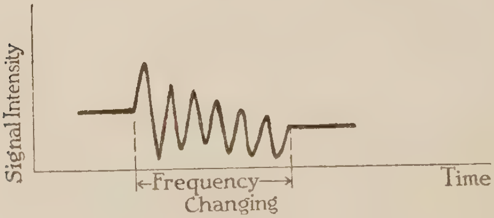

Fig. 4*c*.

(3) *Measurement of Reflection Coefficient of the Ionised Layer.*

(*a*) *Theoretical Considerations.*

In order to define a quantity which will be a measure of the total absorption suffered by the atmospheric wave in its passage from the transmitter to the receiver, it is convenient to assume that the atmospheric deviation takes place suddenly at the surface of an imperfectly reflecting layer situated at a height equal to the measured equivalent height. The reflection coefficient which must be attributed to this ideal layer, in order to account for the observed facts, will serve as an index of the absorption, and will be spoken of as " the reflection coefficient of the ionised layer." This picture of deflection at the surface of an imperfect reflector is only introduced as a convenient method of defining the reflection coefficient, and it must not be supposed that the deviation necessarily takes place in this way.

In order to obtain an estimate of the reflection coefficient it is necessary to know (1) the intensity of the waves starting out in an upwards direction from the transmitting station towards the ionised layer, (2) the intensity of the waves coming down to the ground after deviation by the layer, and (3) the total distance travelled by the waves during their journey to the layer and back. In the present series of experiments two methods of measuring the intensity of the downcoming wave were employed. One of these depended on observations of the naturally occurring variations of signal intensity, known as "fading," and will be called the "natural fading method;" the other method made use of the artifice of making a frequency change at the transmitter, and will be called the "frequency-change method." The two methods will be discussed separately, and in each case it will be shown how the above quantities (1), (2) and (3) are measured or estimated.

(i) *The Natural Fading Method.*—In this method the ratio of the intensity (H_1) of the downcoming wave to the intensity (H_0) of the ground wave, was determined by observations on "fading," and the absolute value of H_0 was measured separately, during the day, when H_1 was of negligible intensity compared with it. From these two results the intensity (H_1) of the downcoming wave was deduced.

It was assumed that the waves returned from the upper atmosphere were deviated comparatively sharply at a height of 100 km. (E region), which we know is the case for waves of 400-metres wave-length.* It is then possible to calculate the total distance (D_1) which the atmospheric wave travels in its journey from transmitter to receiver, and also the angle of elevation θ at which these waves leave the transmitting aerial. Then, if the effective height of the transmitting aerial is h, and the aerial current is I, the intensity of the downcoming wave at the receiver is given by

$$H_1 = ChI \cos\theta / D_1 \qquad (1)$$

if the layer is a perfect reflector. C is here a numerical constant which is derivable theoretically.† If, however, the layer has a reflection coefficient ρ then we have

$$H_1 = ChI \cos\theta \,.\, \rho / D_1, \qquad (2)$$

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* The wave-length used here was 491 metres, *vide* p. 150.

† If H_1 is measured in dynes per unit pole, I in amperes and h and D_1 in metres, C is equal to $0 \cdot 4\,\pi/\lambda$, where λ is the wave-length in centimetres.

so that

$$\rho = \frac{H_1}{H_0} (H_0) \frac{D_1}{ChI \cos \theta}. \tag{3}$$

The calculation of the reflection coefficient from (3) involves a knowledge of the transmitter aerial height and aerial current.

As mentioned above, the ratio H_1/H_0 was obtained from the observations on "fading." The signals were received with a loop antenna, for which the signal is proportional to the magnetic field in the waves. For the wave-length used, the downcoming waves, with magnetic intensity H_1, are reflected at the ground with reflection coefficient approximately equal to unity, and with no phase change, so that they produce an e.m.f. in the loop proportional to $2H_1$. The direct, or ground, wave, with magnetic intensity H_0, produces an e.m.f. in the loop proportional to H_0. Natural variations in received signal strength are due to alterations in the interference system produced by the downcoming ray (H_1) and the ground ray (H_0).

It is known* that the intensity H_1 of the downcoming ray, and the phase difference (ϕ) between the two rays, are continually changing, and at any instant the resultant signal strength is given by the expression

$$\sqrt{(H_0^2 + 4H_1^2 + 4H_0H_1 \cos \phi)}.$$

Thus the resultant signal intensity may change from instant to instant because of either a change in the value of H_1, or a change in the value of ϕ. If the intensity (H_1) of the downcoming wave decreases to zero we observe a change of received signal strength from $\sqrt{(H_0^2 + 4H_1^2 + 4H_0H_1 \cos \phi)}$ to H_0 and we therefore are not able to deduce the magnitude of H_1, since we have no knowledge of the phase angle ϕ. If, however, the change in signal strength is due to a change of the phase angle ϕ, while the intensity H_1 remains constant, we see that the resultant signal intensity will change from a maximum value $H_{\text{max.}}$ given by $H_0 + 2H_1$, to a minimum value $H_{\text{min.}}$ given by $H_0 - 2H_1$, as ϕ changes through 180°. If, therefore, we assume that the change of signal strength with which we are concerned is due to a "phase fade" of this kind, we can determine the ratio $2H_1/H_0$, for it is given by

$$(H_{\text{max.}} - H_{\text{min.}})/(H_{\text{max.}} + H_{\text{min.}}).$$

It is not always easy to decide whether a given change of signal strength is due to a "phase fade" or due to an "intensity fade," but in making the decision we may be guided by the following considerations :—

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* 'Roy. Soc. Proc.,' A, vol. 115, p. 305 (1927).

(α) During a complete "phase fade" of the kind described the signal strength should pass from an extreme value, through the mean value as averaged over the whole record, to an extreme value on the opposite side of the mean. The increase above the mean value should be equal to the decrease below the mean, so that $H_{max.} + H_{min.}$ should be equal to $2H_0$ and should have the same value for all variations observed throughout the evening. Those "fades" for which it differs appreciably from the general mean value, averaged throughout the evening, are rejected in the calculations.

(β) "Intensity fading," due to variation in H_1, will, in general, show a smaller variation of signal strength than "phase fading" since the extremes of intensity will be given by $\sqrt{(H_0^2 + 4H_1^2 + 4H_0H_1 \cos \phi)}$ and H_0. This type of fading also will produce a variation of signal strength which is not symmetrical about the general mean value of signal strength.

If we bear these points in mind it is generally possible to decide, from a "fading curve" which of the "fades" are "phase fades" of the desired type. From the maximum and minimum values of these intensity variations it is now possible to find H_1/H_0. This method of calculation of necessity lays the greatest stress on the large values of H_1, since we must confine our attention to the largest variations of signal strength in order to be certain that the phase angle ϕ is zero at its extremes. The method would therefore be expected to yield a maximum value for the reflection coefficient rather than a mean value.

(ii) *The "Frequency change" Method.* When using the frequency change method to measure the equivalent height of the ionised region we are always able to deduce the ratio of the intensities of the downcoming and the ground rays directly from the photographic records. In this case there is no doubt as to the phase relation between the two rays, and we know that a signal maximum indicates the sum of the two intensities and that a signal minimum indicates their difference. The ratio of the two intensities is therefore given by

$$\frac{H_1}{H_0} = \frac{1}{2} \frac{H_{max.} - H_{min.}}{H_{max.} + H_{min.}}. \tag{4}$$

When this method of determining H_1/H_0 is employed we have the further advantage that the photographic records themselves give us the equivalent height at which deviation takes place, and hence the total distance travelled by the atmospheric wave. In this way it has been possible to investigate separately, the reflection coefficient of waves returned from the E and from the F regions.

In this series of experiments the effective aerial height and aerial current at the transmitter were not known, and it was therefore necessary to adopt a method of calculation slightly different from that described above. If the effective height of the aerial is h, and the transmitter current is I, then, as we have seen above, the intensity of the downcoming wave is given by

$$H_1 = ChI \rho \cos \theta / D_1. \tag{5}$$

The intensity of the ground wave is correspondingly given by

$$H_0 = ChI K/D_0, \tag{6}$$

where D_0 is the distance travelled by the ground ray, and K is the attenuation factor, representing the decrease in intensity due to the fact that the wave has travelled over the surface of the earth. Combining these two expressions we obtain

$$\rho = \frac{H_1}{H_0} \frac{D_1}{D_0} \frac{K}{\cos \theta}. \tag{7}$$

We therefore see that our measurements enable us to calculate ρ if we can estimate the attenuation factor for the ground waves. This attenuation factor can be estimated from the known conductivity of the ground, by an application of Sommerfeld's theory,* if the ground is of a sufficiently uniform character. In the present case part of the transmission distance was over the congested area round London, and the attenuation due to this area is difficult to estimate. From the measurements of Barfield† in this area, there is reason to believe that, for the 400-metre wave which we have used, the error introduced by neglecting this extra attenuation is small.

(*b*) *Experimental Observations.*

(i) *Natural Fading Method.*—The transmitter used was the B.B.C. broadcasting station (5GB) at Daventry, working on a wave-length of 491 metres. Four receiving stations were erected at Retford, Doncaster, Aberford and Topcliffe (near Thirsk) at distances respectively of 122 km., 143 km., 178 km., and 215 km. from Daventry, and as nearly as possible in a straight line. To make the results comparable the receiving assemblies used at the four stations were identical, each consisting of a frame aerial,

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* 'Ann. Physik,' vol. 28, p. 665 (1909).

† 'J. Elect. Eng.,' vol. 67, p. 263 (1929).

4 feet square, connected to a high-frequency amplifier, the output of which was measured by a balanced valve rectifier and galvanometer. In order to calculate the reflection coefficient it was necessary to know the relation between the signal e.m.f. induced in the loop and the deflection of the galvanometer, in the case of each of the sets. All the amplifiers were therefore calibrated by means of a local oscillator, and it was found, in all cases, that the galvanometer deflection was proportional to the square of the impressed signal electromotive force.

Simultaneous records of the variation of galvanometer deflection with time were made at the four receiving stations. The records lasted for a period of 10 minutes, and were separated by intervals of 20 minutes. During the period of sunset continuous half-hour records were made.

The intensity of the ground ray signal received at mid-day was measured for us at each receiving station, the day after the observations (*i.e.*, on April 21, 1928) by B.B.C. engineers, by the kind arrangement of Captain P. P. Eckersley, the Chief Engineer of the Corporation. Observations were taken on two successive days, April 19 and April 20, 1928. On both occasions it was found that the signal intensity was fairly constant at all the stations until sunset occurred. Within a few minutes of the occurrence of sunset, the signal intensity began to vary, and "fading" set in. The fading observed during the first hour after sunset showed, on both occasions, peculiarities which were not observed later in the evening. This "sunset fading" was of a very regular periodic nature and suggested a continuous variation of the phase difference between the ground and the atmospheric waves. During this period the intensity of the downcoming wave was gradually increasing at all stations. This increase of reflection coefficient seemed to be complete in about an hour, and after this time had elapsed, the intensity showed variations but did not appear to be increasing in average magnitude. We therefore restrict our calculations to this second steady period.

Calculating in this way we arrive at results for the reflection coefficient which are shown in Table IV. The reflection coefficient for the night of April 20 was greater, at all observing stations, than that for April 19. It is to be expected that the condition of the ionised regions of the atmosphere will vary greatly from day to day, thus leading to a large variation of reflection coefficient, and it must be emphasised that, although we believe the reflection coefficients of Table IV to be typical of these distances and wave-lengths, they are based on only two nights' observations, and cannot be expected to correspond to the mean value observed under all conditions. Although the actual magnitude

Table IV.

Distance between sending and receiving stations in kilometres :		122.	143.	178.	215.
Values of H_1/H_0	April 19, 1928	0·041	0·10	0·22	0·29
	April 20, 1928	0·09	0·35	0·31	0·29
Reflection coefficient of E region	April 19, 1928	0·070	0·045	0·069	0·058
	April 20, 1928	0·15	0·15	0·09	0·07

of the reflection coefficient may vary from day to day, we feel that the results can be relied on as indicating the nature of the variation of reflection coefficient with distance of transmission.

(ii) *Frequency-change Method.*—As a typical case of the measurement of the reflection coefficient by the frequency-change method we may take the results obtained on March 10, 1928, during the experimental run previously described (p. 137). We assume that the amplifier detector units employed at both stations had a square-law characteristic, since calibration with a local oscillator has always shown this to be approximately the case. It is then found that, considering only cases of reflection at the E region, the values of H_1/H_0 remain approximately constant until 6.45, and then begin to decrease. For the period before 6.45 the mean value of this ratio for all the photographs on which the E region is recorded is found to be 0·25 for Peterborough, and 0·052 for Cambridge. Similarly the values of the ratio for the photographs which show the F region in action are 0·11 for Peterborough, and 0·04 for Cambridge. These figures lead to the following values for the reflection coefficients for the particular wave-length (viz., 400 metres) :—

Cambridge (distance 91 km.)	E region	0·10
	F region	0·26
Peterborough (distance 131 km.)	E region	0·17
	F region	0·24

It will be seen that the value of ρ obtained at Peterborough for reflection at the E region, are of the same order as those obtained by the other method at Retford (distance 122 km.) using a not very different wave-length (491 metres).

In measuring the reflection coefficient we assume that the intensity of the ground ray remains constant and has the same value in the night and in the day. It has sometimes been suggested that the intensity of the ground ray is different in darkness and in sunlight, and it therefore seemed advisable to investigate this point while making the frequency-change experiments. The intensity of the ground ray is derivable at once from the "fringe" photographs, as it is given by $\frac{1}{2}(\mathrm{H}_{\max.} + \mathrm{H}_{\min.})$. This quantity was observed throughout the transition period from night into day, by calibrating the amplifier assembly at intervals by means of a local calibrated oscillator. The results demonstrate that, to the order of accuracy of the calibration, the intensity of the ground ray remained constant, and any small variations which were observed, took place at irregular intervals, and showed no correlation with the incidence of sunlight, so that they seemed to be due to irregular experimental errors rather than to real changes in the ground ray intensity. Our original assumption is therefore justified for the particular wave-length we have used.

(4) *Discussion of Results.*

Before discussing the experimental results described above it seems of interest to consider first what types of variation of equivalent height and reflection coefficient with distance of transmission are to be expected on theoretical grounds. To discuss this general problem in terms of the magneto-ionic theory of refraction would be very difficult, but perhaps the results which have been obtained for certain special cases, in which the effects of the Earth's magnetic field is ignored, may serve as a guide. We shall consider two ideal cases in which the ionisation is supposed to be zero up to a certain height h above which it increases. In case (α) we consider the ionisation as increasing proportionally with the height above h, while in case (β) we consider the ionisation to increase as the square of the height above h. For such cases it may be shown* that:—

$$\text{Case } (\alpha) \quad \text{Equivalent height} = h + h_1 = h + \mathrm{A}\cos^2\theta_0/\lambda^2, \tag{1}$$

$$\text{Case } (\beta) \quad \text{Equivalent height} = h + h_1 = h + \mathrm{B}\cos\theta_0/\lambda, \tag{2}$$

where θ_0 is the angle of incidence of the waves at the lower boundary of the layer, λ is the wave-length in air, and A and B are constants depending on the rate of variation of ionisation with height. We thus see that, in both cases, the equivalent height decreases with increase of θ_0, that is with increase of distance between sending and receiving stations.

The attenuation suffered by the waves in the process of deviation may also be calculated. This quantity in these ideal cases evidently determines the reflection coefficient ρ as defined in Section (3). If we assume that the bending is sufficiently sharp for the variation of atmospheric pressure with height to be negligible (in which case τ, the time between two collisions of an electron with gas molecules, may be considered as independent of the height above h) we have: —

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* 'Proc. Phys. Soc.,' vol. 41, p. 54 (1928).

Case (α) $\rho = e^{-x}$, where $x = A^1 \cos^3 \theta_0/\tau\lambda^2$; and

Case (β) $\rho = e^{-y}$, where $y = B^1 \cos^2 \theta_0/\tau\lambda$.

Here A^1 and B^1 are constants depending on the rate of variation of ionisation with height. We see therefore that in both cases the reflection coefficient increases with increase of distance between the sending and receiving stations.

We now turn to consider the experimental evidence in the light of these theoretical results for ideal cases, and consider first the question of the variation of equivalent height with distance. The experimental results show that there is no very marked and definite variation of equivalent height with angle of incidence. On occasion (*e.g.*, Test No. 49, p. 137, and Test No. 53, p. 140) the equivalent height has been found to decrease with increase of θ_0, a result agreeing with (1) and (2), but such a variation has not been very marked. Moreover there have been cases in which the variation of equivalent height with distance has been in the opposite sense (*e.g.*, Test No. 50, p. 137). Now in our experiments it is known that for the most distant stations θ_0 is, for deviation by E region, about 30° while for the London station it must be approximately 0°. We thus have a variation of $\cos \theta_0$ only from 0·86 to 1 for which case (1) and (2) show that a marked variation of the equivalent height with θ_0 is not to be expected unless h_1 is a large fraction of $h + h_1$.

Formulæ (1) and (2) suggest that, to get some idea of the relative magnitudes of h_1 and h, it would be better to vary the wave-length and not the angle of incidence. Experimentally it is possible to vary the wave-length by a factor of about 4 and still keep the conditions comparable. For such a variation of wave-length it will be seen that in case (α) we have a 16-fold variation of the magnitude of h_1 while in case (β) the corresponding variation would be 4-fold. To obtain evidence on this point simultaneous observations were made at all three receiving stations using both 400-metre and 100-metre waves. These observations, which will be discussed more fully in a subsequent paper, showed at all stations the same variation of equivalent height with wave-length, the height of E region being 125 km. for 100-metre waves and only 92 km. for 400-metre waves. The sense of this variation is such as would be predicted from (1) or (2).

The experimental results in the case of the simultaneous measurements of the reflection coefficient show no marked variation of ρ with the angle of incidence, the experimental values being surprisingly equal. In this connection it should be noted that $\cos \theta_0$ varied from $0 \cdot 86$ for the nearest receiving station to $0 \cdot 68$ for the station furthest away. Now if ρ is of the order of $0 \cdot 1$, as the experiments show, x (or y) is about $2 \cdot 3$. A change of $\cos \theta_0$, even if so small as from $0 \cdot 86$ to $0 \cdot 68$, will, in either case (α) or case (β), change the value of x (or y) by at least 50 per cent., and such a change would cause a very appreciable alteration in ρ. We therefore find a discrepancy between experiment and the simple theory of ionic refraction in a medium in which the ionisation increases steadily with height and in which the frequency of collision of electrons with molecules is independent of the height. We believe that this discrepancy is due to the fact that the variation of τ with height has not been taken into account, and that, in reality, marked absorption takes place in regions below those in which the main deviation occurs. Thus, if an absorbing zone exists below the sharply refracting region (E), the reflection coefficient will be largely determined by the distance which the wave has to travel through this absorbing region. The waves which travel to the more distant receiving stations pass through this layer more obliquely, so that their path in it is longer, and they suffer more absorption. As regards the sharp deviation at the E region, however, we have seen that the reflection coefficient is less for the more distant receiving stations than it is for the near ones. We hence have two effects in operation, one tending to make the reflection coefficient increase with distance, and the other tending to make it decrease, and we might expect that the final result would be that the coefficient would not show any marked variation with distance, as is actually found to be the case. We therefore attribute the result of the small variation of the reflection coefficient with distance, to the influence of an absorbing zone (D region) of ionisation situated below the region (E region) in which the main bending takes place.

It should, however, be added that, according to the theory of ionic refraction, passage through an ionised region takes place with a group-velocity less than that in free space. If, therefore, we have an absorbing region of ionisation underneath the E region, as we have supposed, then we should expect the passage of the rays through the lower ionised region to take place with a lowered group velocity. This would increase the equivalent path, and hence would make the equivalent height large. We have seen that the rays which travel to the more distant receiving stations have a longer path through the D region, and this would tend to make them indicate a greater equivalent height.

Here again, then, we have two conflicting effects, one tending to make the distant stations show the greatest, and the other tending to make them show the least equivalent height. Actually, although the observed variation of equivalent height with distance has been small, a detailed examination of our data shows that the most frequent type of variation is that in which the equivalent height increases with distance. A good example of this type of variation occurred in Test No. 50 on March 10, 1928, as already described on p. 137. Reference to fig. 1 shows that, on this occasion, just after the re-formation of the E region at 6.07½ all stations record the same equivalent height, but that the measured heights afterwards arrange themselves so that the most distant station records the greatest height. This is exactly what we should expect if we remember that during this period the absorbing (D) region is building up underneath the E region, as is evidenced by the decreasing intensity of the downcoming wave as observed at all stations. Possibly the same kind of effect may be taking place during the period between 5.20 and 6.00 a.m. It may be that, at any rate during the latter part of this period, the ionisation is building up in the E region in sufficient intensity to cause a retarding effect of the kind described above. This would lead to greater equivalent heights being recorded by the more distant stations, as is actually observed. This building up of the E region would not necessarily lead to any appreciable absorption, because at these heights the atmospheric pressure is very low and the effect of collisional friction is small. When the ionisation in the E region reaches a certain density, deviation will begin at the E region instead of at the F region. This is the sequence of events which is actually observed.

We now turn to consider the bearing of the simultaneous equivalent height measurements on the problem of the penetration of the E region. When observations at the single receiving station at Peterborough had shown that large values of the equivalent path difference between the ground and atmospheric waves often occurred, two possible explanations could be given. The large equivalent path difference might be due to an atmospheric ray which had been twice reflected at the E region, and once reflected at the ground, at a point half-way between the transmitter and receiver, or it might be due to a ray which had been reflected once from a still higher F region. When the simultaneous observations were planned it was thought that the Cambridge station was situated sufficiently near to the middle point of the transmission path between Teddington and Peterborough to enable a decision to be made between these two explanations. The experimental data under review show that, on the nights when abnormally large equivalent paths have been experienced, they have been recorded at all three stations. The results therefore leave little doubt that on these occasions E region was penetrated by the waves which were then reflected by a still higher region F which was richer in ionisation. Moreover it was found that, on the nights in question, the re-formation of E region on the advent of sunrise was observed at about the same time by all three stations. Actually the most distant station recorded re-formation of E region first and the nearest station last, but the whole period of transition has not been found to be much longer than, about 20 minutes. Such a variation in the sequence of events at different distances is what we should expect according to any theory of reflection or refraction of the waves by E region.

Further evidence in connection with this question of the interpretation of the large equivalent paths is available in the measurement of reflection coefficients which have been made at the Peterborough and Cambridge stations. For both stations it is found that the reflection coefficient is greater when the larger equivalent path is recorded than it is when the shorter equivalent path is observed. If the long equivalent path was due to a double reflection from the E region we should expect the effective reflection coefficient to be equal to the square of that observed for the shorter equivalent path. Actually it is found to be greater, and from this we conclude that the waves have not suffered a double reflection. We can see the reason for the larger reflection coefficient for the F region if we remember that at these heights the collision time (τ) of an electron is considerably less than it is in the case of the E region.

Observations on the angle of incidence of downcoming waves at Peterborough have also indicated abnormally large equivalent height during the periods when E region has been penetrable. On these occasions the value of sin θ_0, where θ_0 is the angle of incidence of the downcoming waves at the ground, has been about 0·3, instead of the more usual value of 0·5 for E region. For such cases of reflection by F region, however, there does not seem to be the same agreement between the equivalent heights obtained using the two methods (frequency-change method and angle-of-incidence method) which have been employed at Peterborough. In this connection it may be mentioned that a fair agreement is normally found for cases of reflection by E region. While it is certainly possible that this lack of agreement in the case of F region might be partly due to experimental errors, for the determination of the angle of incidence is particularly difficult when the angle of incidence is small, there seems a definite possibility that the difference is real and of physical significance. It seems not improbable that we should picture both E and F regions as containing irregularities comparable in size with the wave-lengths we are using, so that a certain amount of diffuse or irregular reflection or refraction is likely. Such irregularities would cause lateral deviation of the waves which would be most evident in wireless observations when the angle of incidence on the reflecting region is small. It is easy to show that such lateral deviation would, in the case of the aerial and loop comparison used in the measurement of angle of incidence, tend to reduce the effect of the downcoming waves in the loop relative to the effect on the aerial, thus making the measured angle of incidence too large. The experiments may therefore be interpreted as suggesting that lateral deviation is more marked for cases of reflection by F region than for cases of reflection by E region. Experiments using the Adcock direction finder would settle this point.

(5) *Summary.*

Simultaneous measurements of the equivalent height and reflection coefficient of the ionised layer for 400-metre waves have been made at different distances from a wireless transmitting station. The equivalent height was found not to vary markedly with the distance between the transmitting and receiving stations. Additional evidence of night-time penetration of the Kennelly-Heaviside layer (E region) by 400-metre waves has been found. On such occasions, after reflection has taken place from a still higher region F, the re-formation of E region is observed practically simultaneously at different receiving stations.

The lack of marked variation of the reflection coefficient of the layer with angle of incidence, which has been found experimentally, is interpreted as indicating the existence of an absorbing zone situated at a lower level in the atmosphere than the region responsible for the deviation of the waves.

(6) *Acknowledgments.*

The work described in this paper was carried out as part of the programme of the Radio Research Board and is published by permission of the Department of Scientific and Industrial Research. The authors gratefully acknowledge their indebtedness to their collaborators, whose names are mentioned in the paper, and also to Captain P. P. Eckersley, formerly Chief Engineer of the British Broadcasting Corporation for his ready co-operation on many occasions.

On some Short-Wave Equivalent Height Measurements of the Ionized Regions of the Upper Atmosphere.

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(Received March 13, 1930.)

[Plates 2, 3.]

1. *Introduction.*

The present paper continues the account of wireless investigations of the ionized regions of the upper atmosphere given in two previous papers.* The results discussed in it consist chiefly of measurements of the equivalent heights of the ionized regions made simultaneously at two or three receiving stations with wave-lengths of the order of 100 metres. The frequency-change method of measuring the equivalent height was used throughout.

2. *Extension of Equivalent Height Measurements to the Use of Short Waves.*

The experiments described previously were continued with shorter wave-lengths with two objects in view. In the first place it had been found that 400-metre waves penetrated the lower ionized region (E region) only on certain nights, and then only during the few hours before dawn. This result clearly showed that penetration of this region was most likely when the density of ionization was least. But, according to most theories of wireless propagation, a greater electronic density is required to reflect or refract short waves than is the case with long waves, so that it was anticipated† that by reducing the wave-length below 400 metres it might be possible to penetrate E region over a longer period of time during the night than had been possible when 400-metre waves had been used. In this way it was hoped to make a more detailed study of the variation of the equivalent height of the upper region (F region) which had been found to reflect 400-metre waves on the occasion when they had penetrated the normal E region. Secondly, since it is known that the attenuation of the ground waves increases rapidly as the wave-length is reduced below, say, 400 metres, it was expected that, with the use of shorter waves, the ratio of the values of downcoming wave intensity and ground wave intensity would be much increased at all stations. Such an increase, it was expected, would make it possible to continue the measurements of equivalent heights, in general, a good deal further into the daylight hours. Such daylight measurements on longer waves had previously been found difficult, because of the relative weakness of the intensity of the downcoming waves as compared with that of the ground waves.

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* 'Roy. Soc. Proc.,' A, vol. 126, p. 452 (1930), and vol. 128, p. 133 (1930).

† 'Nature,' vol. 120, p. 330 (1927).

3. *Experimental Arrangements.*

The transmissions were again provided by arrangement with Dr. Smith-Rose from the National Physical Laboratory (5HW) and were carried out for us by Messrs. E. L. Hatcher and A. C. Haxton. The sending station consisted of a self-excited valve oscillator feeding an aerial consisting of a single elevated wire. Through the courtesy of Dr. D. Dye accurate measurements were made of the mean frequency emitted and the magnitude of the frequency changes used for producing the necessary succession of interference phenomena at the receiving stations. The mean frequency f and the frequency change Δf varied slightly from test to test, but as the latter was known accurately the results are strictly comparable. A typical case was one in which the mean frequency f was 3008·3 kilocycles per second, corresponding to a wave-length of 99·4 metres, while the frequency change Δf used was one of 18,500 cycles per second, corresponding to a change of 0·617 metre. For a succession of Δn interference maxima or minima produced by two sets of waves, the equivalent path-difference $P_1' - P_2'$[*] of the two wave tracks is given by

$$P_1' - P_2' = c\,\Delta n/\Delta f, \qquad (1)$$

c being the velocity of radiation in free space. In the particular case mentioned we therefore have

$$P_1' - P_2' = 16\cdot 2\,\Delta n \text{ km.} \qquad (1\text{A})$$

The receiving stations were, as before, situated (A) at King's College, London; (B) at the Radio Research Board Hut, near the C.U.O.T.C. Rifle Range at Cambridge; and (C) at the Radio Research Board Station, Dogsthorpe, Peterborough. The three stations were manned by the same personnel as in the earlier series of experiments, except that Mr. L. G. Vedy took the place of Mr. W. L. Shaw at the Cambridge Station.

The wireless receivers used at first at each station consisted of a super-

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[*] As in previous papers we distinguish between an equivalent path P′ and an optical path P of the atmospheric waves. The relation between the two is given by

$$Pf = \int_0^f P'df.$$

heterodyne circuit, the first stage of which was a self-excited oscillator, which both produced the heterodyne and effected the frequency conversion to a value appropriate for the remaining amplifying stages. Since it was necessary for the receiver to be responsive over a rather large band of frequencies the intermediate frequency amplifier contained only one tuned circuit. Trouble was, however, encountered with atmospherics and telegraphic signals at the intermediate frequency used, so that, when screened-grid valves became available, the use of amplification at high frequency, without frequency conversion, was again adopted. A cascade of two screened-grid valves, when used with a damped aerial system, provided uniform amplification over a range of about 20,000 cycles per second.

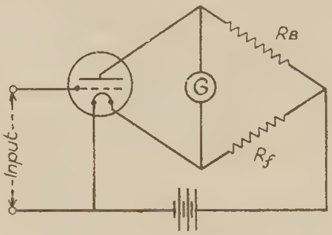

FIG. 1*a*.

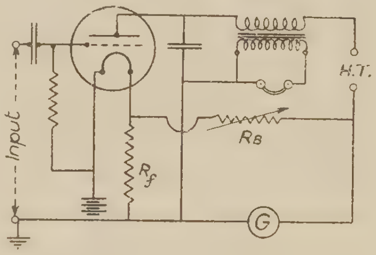

FIG. 1*b*.

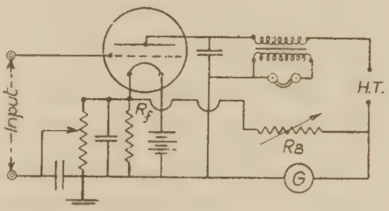

FIG. 1*c*.

The output of the amplifier was measured by means of a rectifying system working in conjunction with a Cambridge string galvanometer. Owing to the large and frequent changes of signal amplitude experienced at Peterborough and Cambridge it was found necessary to have ready to hand, at each station, a continuously variable resistance shunted across the galvanometer. Under these conditions the crystal rectifier used at first was liable to serious over-loading, which caused a serious deterioration of its rectifying properties. In view, therefore, of the importance of reliability in connection with the schedule work of the three receiving stations it was decided to substitute a valve rectifier in place of the crystal rectifier. To find the best compromise between sensitivity, constancy of operation, and safety, when used with a delicate galvanometer, required a fairly exhaustive investigation of valve rectifier circuits. The basic principle of the circuit finally evolved in this connection is illustrated in fig. 1 (*a*), where the filament resistance and the anode-to-filament space resistance of the valve are balanced with two other resistances R_f and R_B in a Wheatstone's bridge assembly. The practical applications of this fundamental circuit for cumulative grid rectification and anode-bend rectification are illustrated in figs. 1 (*b*) and (*c*) respectively, where the usual wireless circuit conventions have been employed. For the former circuit a valve with a high mutual conductance is suitable while for the latter a high amplification-factor valve is found best. It should be noted that a break in the filament of any of these circuits brings about the cessation of both steady anode and balancing currents simultaneously so that no damage is done to the galvanometer. The rectifier almost invariably employed in these measurements was the one illustrated in fig. 1 (*b*).

As with the tests on longer wave-lengths, the arrangement usually adopted was to have a series of 10 frequency-changes made at the transmitter once every 10 (or 7½ or 5) minutes. Each of the 10 frequency-changes was made uniformly during a period of 3 seconds, there being a pause of 2 seconds between any two consecutive changes.

4. *Experimental Results and Discussion.*

As the data obtained in the complete series of these experiments is rather voluminous, a selection of typical observations has been made which illustrate most directly the main results of the work.

(*a*) *The Diurnal Variation of Equivalent Height.*—The first series of observations on short waves was made at King's College on the morning of August 28, 1928, when it was found, as had been anticipated, that the signal variations artificially produced by the frequency-change were specially marked, making the counting of the interference maxima on the records a relatively easy matter. At the same time it was found that the equivalent heights recorded were very much higher than those observed with the longer wave-lengths during the sunrise period. For example, although sunrise occurred at 5.5 a.m.* heights of from 260 to 240 km. were recorded up till 7.10 a.m. These observations are to be compared with those on 400 metres for which it was always found that by sunrise the equivalent height was about 100 km., the ionization in E region having become so dense that it was no longer penetrable. Since it was, therefore, fairly clear that 100-metre waves were penetrating to F region even 2 hours after sunrise, a series of observations were made still later in the day on October 15 and October 17, when the ionization in E region might be expected to be most intense and the conditions most favourable for the reflection by it of short waves. Between 11.15 and 11.45 a.m. on October 15 the equivalent height was found to be 136 km., while for the same period on

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* All times are given in G.M.T.

October 17 it was as low as 89 km. It is noteworthy in this connection that there was a magnetic storm on the latter date.

As there was reason to believe that both these heights were to be associated with E region, it was considered that the discontinuity between reflection at the upper region and reflection at the lower region had occurred some time between sunrise and mid-day. It was, therefore, decided to carry out a continuous run of observations embracing as much as the 24 hours as was possible with the personnel available, the chief aim in view being to obtain the times at which the lower region just began and just ceased to reflect 100-metre waves. Simultaneous and continuous observations were made at all three stations for a period of 17 hours* on Sunday, October 21, 1928, that day of the week being chosen to obtain conditions at King's College as free from local electrical interference as possible.

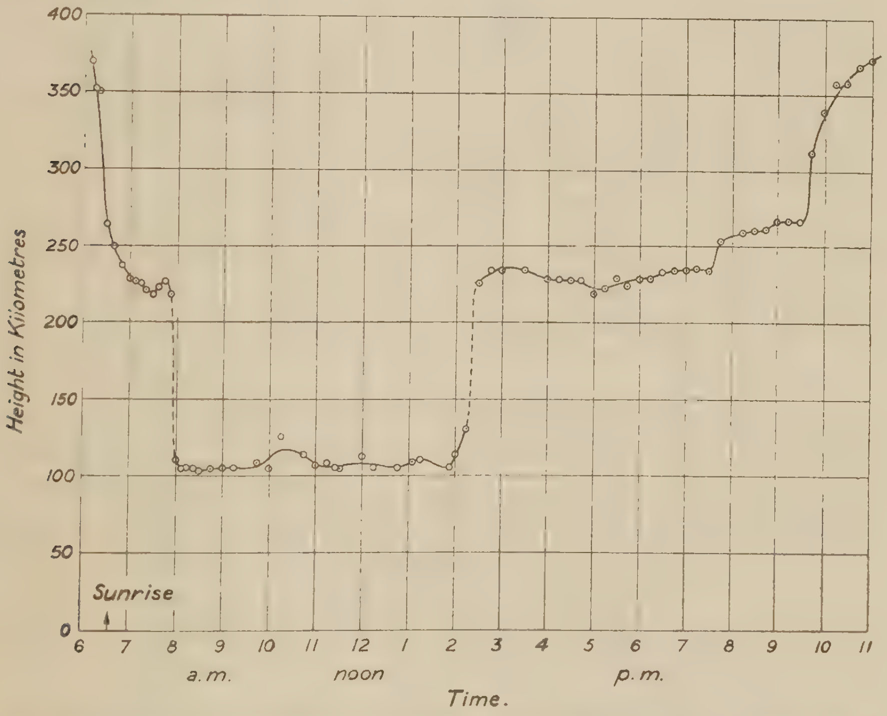

Fig. 2.—Showing variation of equivalent height as measured at King's College (London) on October 21, 1928. Wave-length 100 metres; distance of transmission 18 km.; sunrise 6.34 a.m.; sunset 4.55 p.m.

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* In this connection we are specially indebted to Mr. C. W. Oatley and Mr. R. A. L. Borrow who gave us most valuable assistance at the National Physical Laboratory and King's College respectively.

The results of this particular day are best illustrated by the graph shown in fig. 2, which shows how the equivalent height, as observed at King's College, varied with time.

It will be seen that on the approach of sunrise the equivalent height fell rapidly but after sunrise it tended to an approximately constant value of 225 km. At about 80 minutes after sunrise there was a sharp discontinuity in the series, the record at 7.53 a.m. indicating a height of 220 km. and that at 8 a.m. indicating a height of 110 km. The lower value, with slight variations, was maintained until about 2.20 p.m. (155 minutes before sunset), when another discontinuity in the series of values was obtained and heights of the order of 230 km. were again measured. As the evening advanced the height, while varying somewhat, gradually increased to a maximum value which occurred between 11 p.m. and 6 a.m.

Quite similar results were obtained at both Cambridge and Peterborough, except that the discontinuities in the observed results occurred at slightly different times. This is strikingly illustrated by a comparison of the number of fringes recorded simultaneously at King's College and at Peterborough for the morning discontinuity. These are given in the table below.

Times (a.m.):	7.15.	7.30.	7.53.	8.0.	8.15.	8.30.
King's College (Δn)	27·0	26·0	26·0	12·6	12·0	12·0
Peterborough (Δn)	26	25	14·5	13·0	13·0	13·0

It will be seen that the change from upper series of values to the lower series occurred at Peterborough a few minutes before it occurred at King's College. As the lower series of values was recorded at Peterborough for about an hour later in the afternoon than at King's College, the results as a whole suggest that less ionization is required to give appreciable reflection from E region to a distant station than to a near station. This result is in agreement with theory, and further reference will be made to it below.

(*b*) *Special Investigations carried out during the Period of Sunrise.*—In order to compare the results obtained on 100 metres with the considerable body of data that had been amassed from the early morning experiments on the higher wave-lengths, a series of morning runs were made on November 3, November 17, December 1, December 29, 1928, February 8, and February 22, 1929. Sunrise varied from 6.59 a.m. on November 3 to 8.8 a.m. on December 29, to 7.4 a.m. on February 22. A special object of these sunrise observations was to find out if the formation of E region in sufficient density to reflect 100-metre waves always took place about 80 minutes after sunrise, as had been the case on October 21. Although these morning runs were all continued to at least 2 hours after sunrise, there was only one occasion when the formation of E region was registered at all stations in a way comparable to that observed on October 21. This was on November 17. October 21 and November 17 were, however, exceptional only in that the lower E region was effective as a reflector during a larger fraction of the period of the experiment.

The results of these morning runs are best described by considering first one of the usual cases and the exceptional case of November 17 afterwards. The results of the first morning of this series (November 3) enabled us to make a comparison of the equivalent heights for F region measured simultaneously at the three stations. At first this comparison was made on the assumption that a singly reflected ray F_1 and a ground ray E_0 were being received at all stations, but it was soon found that using this hypothesis no such agreement as had been found for the higher wave-lengths was obtained. The most noteworthy result of the calculations was that the equivalent height thus measured for Peterborough came out higher than the value for King's College. Now for a refracting layer the ionization of which increases with height it has been shown* that if the equivalent height is to vary at all with distance of the observing point from the source we should expect to find a decrease of equivalent height with increase of distance between sending and receiving stations.

An examination of the records at Peterborough suggested a solution of the difficulty. It was found from these records that both the mean signal and the fringe amplitude varied irregularly during a wave-length change, which suggested that both of the sets of interfering waves were downcoming waves. A comparison of the equivalent heights calculated in two ways was therefore made. In the first case (A) it was assumed that interference between a ground ray and a singly reflected ray was taking place. In the second case (B) it was assumed that interference was taking place between a single reflected ray and a doubly reflected ray, the ground ray being absent.

The results of these calculations for the morning of November 3 are given in the table below. As it was considered both from the nature of the records and from the short distance of transmission that a ground wave was being received at King's College, the equivalent heights for that station are given for case (A) only.

The comparison of the cases of King's College and Peterborough will be

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* 'Proc. Phys. Soc.,' vol. 41, p. 54 (1928).

Time of test.	No. of signal maxima (δn).			Equivalent heights (km.) Case A.			Equivalent heights (km.) Case B.	
	Peter-borough.	Cambridge.	King's College.	Peter-borough.	Cambridge.	King's College.	Peter-borough.	Cambridge.
a.m.								
6.40	38	—	34·6	367	—	290	310	—
6.50	35·3	33	33·9	344	310	280	289	272
7.0	33·3	33·25	32·3	330	315	272	274	275
7.10	31·3	30·0	30·1	317	285	253	256	247
7.20	29·1	32·5	28·3	297	305	240	240	265
7.30	29·3	—	28·6	204	—	242	242	—
7.40	29·9	28·3	28·5	305	272	240	245	240
7.50	28·5	24·5	28·6	292	242	242	235	204
8.0	28·9	25·6	27·2	296	250	230	240	214
8.10	27·5	24·5	27·4	285	242	227	235	204
8.15	28·0	22·0	26·6	288	220	225	232	185
8.20	27·5	23·0	26·3	285	230	223	227	193
8.25	26·5	24·0	26·5	275	238	225	220	200
8.30	27·0	21·75	25·2	280	220	214	223	184
8.35	27·3	24·0	24·7	282	238	210	225	200
8.40	28·0	23·0	26·1	288	230	222	232	193
8.45	27·7	22·75	28·0	286	227	237	230	190
8.50	27·2	22·4	26·0	280	225	220	225	188
8.55	26·8	23·6	26·7	276	235	225	224	197
9.0	26·5	23·6	26·0	275	235	220	220	197
9.5	28·5	—	27·5	292	—	232	235	—

considered first. It will be seen from the fifth and third columns from the right that no agreement at all is found for Case A in which interference between a ground ray and a singly reflected ray is assumed. On the other hand if we compare the second and third columns from the right a remarkably good agreement is found. This agreement seems to show that we must consider interference between a ground wave and a singly reflected wave to take place at King's College, whereas at the same time the Peterborough station experiences interference phenomena between a singly and a doubly reflected wave. A reference to another experiment which confirms this interpretation is given below.

In comparing the results of Cambridge and King's College, it is seen that at first better agreement is found by supposing that two downcoming rays are received at Cambridge with a negligible ground ray since the third and first columns from the right agree more closely than do the fourth and third columns from the right. But as the morning advanced it is found that just the reverse is the case and that better agreement is obtained by considering that interference between a ground wave and a singly reflected wave is being experienced at both stations. Such a result is what we should expect, since it is a matter of experience that the strength of all downcoming rays is gradually reduced as the morning proceeds. At first, for the Cambridge site, both the singly and doubly-reflected waves (F_1 and F_2 respectively) were stronger than the ground ray E_0 so that the most marked interference phenomena on the records were the maxima and minima due to F_1 and F_2, F_1 being, of course, the stronger. As the morning proceeded and the sun's rays caused more ionization and thus more absorption in the lower atmosphere, both F_1 and F_2 were reduced in intensity until E_0 (the ground wave intensity) became stronger than F_2. The most marked interference phenomena were then produced by F_1 and E_0, as at King's College. The change over from one set of conditions to the other is considered as taking place on this particular morning at about 7.50 a.m.

It will thus be seen that the Cambridge results are intermediate between those of King's College and those of Peterborough, in that while we find Case A always applying at King's College, Case B applying at Peterborough, and sometimes both applying at Cambridge. As the equivalent height remained approximately constant after 8.15 a.m. we can compare the mean heights measured at the three stations. For the period from 8.15 a.m. to 9.5 a.m. these are :— King's College 223 km., Cambridge 230 km., Peterborough 227 km.

Another way of demonstrating the agreement which is obtained at the different stations is to exhibit graphically the variation of equivalent height

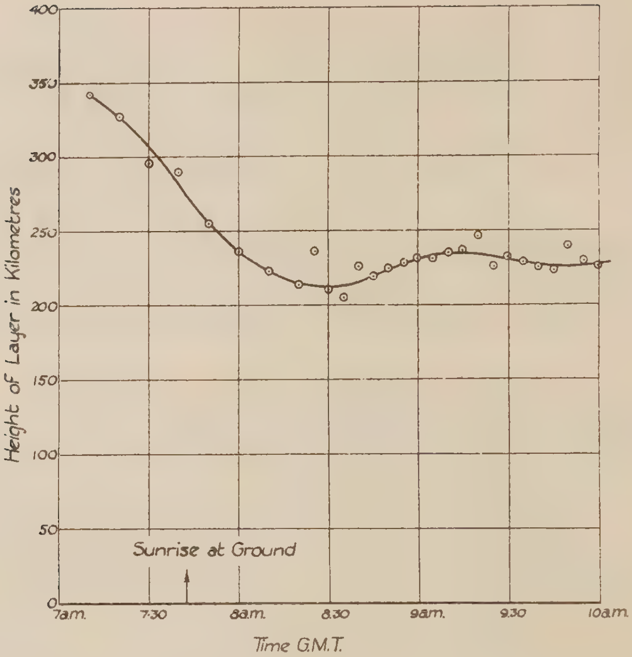

FIG. 3A.

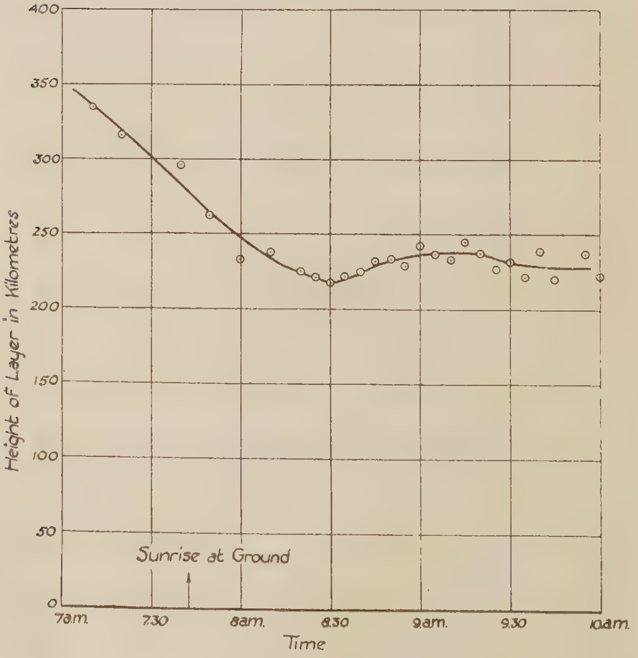

FIG. 3B.

FIG. 3.—Showing variation of equivalent height as measured; (A) at King's College; (B) at Peterborough on Dec. 1, 1929.

with time for the same period. This is done for the morning of December 1 in fig. 3 for the King's College and Peterborough results. There is a remarkable general agreement between the results at the two stations. The equivalent height is seen to fall steadily until about 46 minutes after sunrise when a slight rise took place and afterwards a still smaller fall. It seems probable that this rise in the height of F region is associated with the formation of E region, as the following considerations show. Let us take the case of King's College for which we can regard the reflection from the layer as taking place at practically vertical incidence. What is measured in these experiments is the quantity $c\int\frac{ds}{U}$ for the atmospheric wave, ds being an element of path along which the waves travel with group velocity U. Now although the region E may form in sufficient intensity to cause the value of the group velocity in the medium to be appreciably less than the velocity of light, the ionization in it may not be sufficient to bring about total reflection of the waves. Thus if the rays passing upwards to F region pass through a moderately ionized E region the value of $c\int\frac{ds}{U}$ will be greater than $\int ds$, and the more ionization there is in E region the greater will this difference be. It thus seems reasonable to attribute the rise in the equivalent height of F region not to an increase in actual height but to a reduction in the group velocity of the waves consequent on the increasing ionization in E region. The slighter subsequent fall in the equivalent height of F region is probably either a true fall or an increase in the ionization gradient of this region, due to the more nearly vertical incidence of the sun's radiation.

The early morning run during which the lower region was found to reflect appreciably a short time after sunrise was on November 17, 1928. The results of this particular morning are of special interest because, although the lower region became effective very early (about 39 minutes after sunrise) the upper region was detectable at intervals afterwards. On some of the King's College records signs of only E_1 were found; on others F_1, and, on a few, signs of both E_1 and F_1 could be traced. The result is that it is possible to follow fairly reliably the variation in equivalent height of both layers at the same time. The King's College readings are shown in fig. 4 where it will be seen that, even when reflection from E region is also being experienced, the general trend of the variation in the equivalent height of F region is similar to that experienced on other days (*cf.* fig. 3) when no downcoming rays from E region are being received.

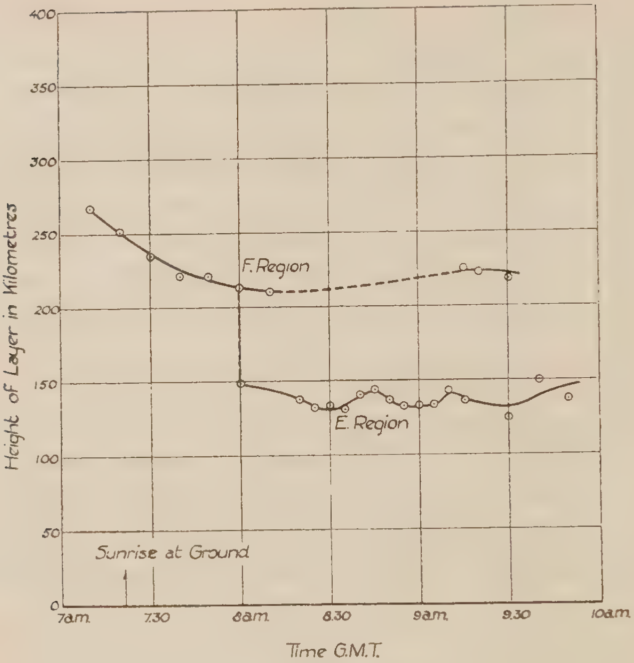

Fig. 4.

(*c*) *Day-time Measurements of Equivalent Heights.*—As it had been found that on certain days E region was penetrable at approximately vertical incidence, even in full daylight, a series of day-time tests were carried out to find out how frequent such days were. These day-time tests were carried out either (*a*) between 11.00 and 13.00 G.M.T., or (*b*) between 14.00 and 16.00 G.M.T. There was no day in this series on which evidence of reflection from E region was obtained at King's College and not at Peterborough. On the other hand there were three occasions (November 30, December 16 and January 24) when E region was registered at Peterborough and not at King's College. This result is what we should expect either in a reflection or refraction theory of deviation of the waves by the layer.

The King's College results show fairly definitely that a more vertical incidence of solar radiation favours the formation of E region in sufficient intensity to reflect 100-metre waves for, during the (*a*) series mentioned above, out of eight runs there were three on which E layer only was recorded, three on which F layer only was recorded, and two days on which both were recorded simultaneously, which results are to be contrasted with the (*b*) series for which, out of eight runs, there were no days on which E layer alone was recorded, four days on which F alone was recorded and four days on which reflection from both was found.

(*d*) *Sense of Layer Movements.*—As has been shown in one of the preceding papers, the frequency-change method may be used to find the rate of change of optical path (dP/dt) of the atmospheric waves when such a change is proceeding steadily. From the natural phase changes preceding and succeeding a frequency-change of known sign, it is possible to infer whether the optical path is increasing or decreasing. Many examples of such natural phase changes have been observed during the early morning hours, when the equivalent height of F region is falling. In all cases the natural phase change has been of the same sign as that produced by a decrease of transmitter frequency. The results therefore confirm the conclusion previously arrived at, from observations on longer waves, that both the equivalent path and the optical path of the atmospheric waves are being steadily reduced during this period.

To find the magnitude of the rate of change of the optical path, as well as the sign, the numbers of fringes produced by increasing and decreasing frequency-changes have been compared. In this connection it has been shown* that, if Δn_1 is the number of fringes produced by an increase of frequency Δf and Δn_2 is the number produced by a decrease in frequency of the same amount, we have

$$\frac{dP}{dt} = \frac{c}{f}\,\frac{\Delta n_1 - \Delta n_2}{2\,\Delta t'}, \tag{2}$$

where $\Delta t'$ is the time interval during which the frequency-changes are made, f the mean frequency and c the velocity of radiation in free space. Using 100-metre waves it has been found that, during the early morning period, when the equivalent height of the layer is steadily falling, there is always a measurable difference between the numbers of fringes for increasing as compared with decreasing frequency-changes. The usual type of test employed consists of a series of 10 alternate increases and decreases of frequency of the same amount, each taking place in about 3 seconds, with 2-second intervals during which the frequency is constant. For example, at 5.40 a.m. on April 26, 1929, in an experiment with 100-metre waves, the number of fringes for the 10 consecutive changes were 31·0, 34·5, 31·1, 32·5, 30·5, 33·5, 30·5, 35·0, 30·0, 35·5. It will be seen that the average number for the odd numbered changes (which were frequency increases of 18,500 cycles per second) is 30·6, while that for the even numbered changes (which were frequency decreases of 18,500 cycles per second) is 34·2. From (2), taking $\Delta t'$ as 3 seconds and f as 3×10^6 cycles per second, we find that $dP/dt = -3\cdot6$ km. per minute.

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* 'Roy. Soc. Proc.,' A, vol. 126, p. 549 (1930).

A discussion of the relation between the optical and equivalent paths for simple types of ionization gradients in the layer has been given by one of the writers,* from which it may be seen that, for short waves impinging on the layer at vertical incidence, the optical path is given by $2h + 4/3\alpha$ and the equivalent path by $2h + 4/\alpha$, h being the height of the lower boundary of the layer above the ground and α a constant. Here the ionization is assumed to increase proportionally with the height above the lower boundary of the layer. For ionization varying as the square of the height above h the optical path is given by $2h + \pi/2\sqrt{\beta}$ and the equivalent path $2h + \pi/\sqrt{\beta}$. Evidently the decreases that take place in both the optical and equivalent paths may be due to decreases in h or increases in α (or β). A decrease in h means that the layer falls as a whole, while a decrease in α (or β) means that the ionization gradient in the layer is increased. An equal decrease in the equivalent and optical paths therefore means a reduction in h, while if the decrease in equivalent path is greater than that in optical path, an increase in the ionization gradient is indicated. In order to compare the reductions in equivalent and optical paths during a definite period, continuous photographic records of signal variations caused by frequency-changes during a 20-minute interval were made on February 8, 1929, and April 26, 1929. The results obtained on the latter occasion at King's College may be taken as typical of the results as a whole. Between 4.50 a.m. and 5.10 a.m. the average difference in the number of fringes for increasing and decreasing frequency-changes was 2·08 fringes. As the frequency-changes took place in from 2·5 to 3·0 seconds, this indicates a steady reduction in the optical path of from 2·1 to 2·5 km. per minute. Now during the same period the equivalent path of the atmospheric waves was reduced at the rate of about 3·0 km. per minute. The results, therefore, show definitely that the reduction in the equivalent path was greater than the reduction in optical path, indicating some adjustment of ionization in the region itself, but the fact that the rates are not so very different indicates most probably that the region also fell to some extent as a whole. Further experimental data, which the method used seems certainly capable of yielding, are required before we can apportion the reduction in the actual height at which the atmospheric waves are reflected to the reduction in h or to the increase in α (or β).

(*e*) *Comparison of Equivalent Heights for Different Wave-lengths.* —In order to compare the results obtained on wave-lengths differing as much as possible, a series of early morning tests was carried out in which a double determination of the equivalent height of the layer was made every 10 minutes, one determination being made with 400-metre waves and the other on 100-metre waves. The two determinations were usually made within a period of about 3 minutes.

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* 'Phys. Soc. Proc.,' vol. 41 (1928). See p. 51, equations (30) and (31).

Of this series the results obtained on May 24, 1929, may be taken as typical. For the 400-metre waves E region only was observed throughout the whole morning period, the post-sunrise value of the equivalent height being about 92 km. for all three receiving stations. For the 100-metre waves, however, F region was registered at all stations during the early part of the test. After sunrise E region formed in sufficient intensity to reflect these waves, the lower series of heights being first registered at 5.40 a.m. at Peterborough, at 5.50 a.m. at Cambridge, and at 6.10 a.m. in London. From about 6.20 a.m. onwards it was therefore possible to compare the equivalent heights of E region for the two wave-lengths. During the period from 6.30 a.m. to 7.10 a.m., the average heights for the two wave-lengths at the three stations was as shown in the table below.

Wave-Length.	Height. King's College, London.	Height. Cambridge.	Height. Peterborough.
metres.	km.	km.	km.
400	93	91	91
100	125	125	120

The results therefore show clearly that the equivalent height for 100-metre waves is greater than for 400-metre waves, indicating that the shorter waves penetrate further into the layer before being reflected than do the longer waves. A further reference to this matter is made below.

(*f*) *Some Typical Records of Interference Phenomena.*—Examples of typical records are reproduced in figs. 5 to 8 (Plates 2, 3). They were all taken with 100-metre waves and show signal intensity as a function of the time.

Fig. 5 was recorded at King's College on May 24, 1929, at 4.20 a.m. (sunrise 3.55 a.m.), and is typical of the results obtained when reflection is being obtained from F region. The frequency-change was the normal one of 18,500 cycles per second.

Fig. 6 was taken on the same day (May 24) at 6.0 a.m., after E region had begun to reflect. As the same frequency-change was used as for fig. 5, the relative numbers of " fringes " shows the relative path differences in the two cases.

Fig. 7 was taken on April 26, 1929, at Peterborough, at 6.50 a.m. (sunrise 4.41 a.m.), and is an interesting illustration of reflection from both E and F regions. In the record taken previously at 6.40 a.m. the number of fringes was about 25·0, while the record taken subsequently showed about 12 fringes. This record shows a mixture of about 25 and 12. The frequency-change was, as usual, 18,500 cycles per second.

Fig. 8 was taken on May 24, 1929, at 5.50 a.m., and is an example showing "phase fading." The first frequency-change was an increase of 18,500 cycles per second, while the second change was a corresponding decrease. The value of Δn for the first change is 14·1, while that for the second is 14·5, indicating that the optical path of the atmospheric waves is decreasing. This is confirmed by the fact that the natural phase changes taking place immediately before and after the first frequency-change are opposite in phase to those produced during the change itself. This record was made at King's College.

5. *Further Discussion of the Experimental Results.*

The results described above support the conclusion, reached in previous papers, that there are two ionized regions in the upper atmosphere which are chiefly responsible for the deflection of wireless waves. The evidence put forward, however, merely shows that these two regions exist at different heights, and does not tell us what type of electrification lies between. Moreover, since the heights measured are equivalent heights, they are greater than the heights of the highest points reached by the atmospheric waves. At first sight it therefore appears as if the evidence does not contribute very materially to the solution of the real problem at issue, namely, the determination of the atmospheric ionic density as a function of the height above the ground. It is, however, possible to make some sort of estimate as to how far the equivalent heights differ from the actual heights in certain somewhat limited cases. Let us consider a case of approximately vertical incidence. We know that the equivalent atmospheric path $c\int\frac{ds}{\mathrm{U}}$ will be greater than the atmospheric path $\int ds$, while the optical path $\int \mu\, ds$ will be less than $\int ds$. If, therefore, we can find both the equivalent path and the optical path we have the limits between which $\int ds$ (which is equal to twice the actual height reached by the waves in the case of vertical incidence) must lie.

After sunrise, when E region is formed in sufficient intensity to reflect

100-metre waves, the average equivalent path of the atmospheric waves varies from 184 km. for 400-metre waves to 250 km. for 100-metre waves. Using these two results and assuming, as a first approximation, that the relation between atmospheric wave equivalent path P′ and frequency is linear, we have

$$P' = P_0' + Af, \tag{3}$$

where P_0' is the equivalent path for zero frequency and A is a constant. The relation between optical and equivalent paths, namely,

$$Pf = \int_0^f P' \, df, \tag{4}$$

becomes in this case

$$P = P_0' + \tfrac{1}{2}Af. \tag{5}$$

Now the two unknowns P_0' and A in (5) can be found when the equivalent paths for two different wave-lengths are known, so that P can be found. For the case of E region in the early morning, using the numerical values given above, the value of P for 100-metre waves is found, in this way, to be 206 km. The actual path for these waves must therefore lie between 206 km. and 250 km., so that the actual height at which 100-metre waves are reflected must lie between 103 km. and 125 km. Now it is known that 100-metre waves require an electron density of about 10^5 electrons per cubic centimetre to reflect them, so that we obtain the result that on many days, at this time in the morning, the ionization density is 10^5 electrons per cubic centimetre at a height of about 110 km. Observations made later in the day often show that the equivalent height for 100-metre waves is as low as 100 km., so that the electron density must have reached 10^5 per cubic centimetre at a height lower than this.

The wave-length of 100 metres appears to have been, by chance, somewhat fortunately chosen, for it seems a critical wave-length in that on some days waves of this length will penetrate E region, while on others they are reflected by the same region. The wave-lengths of 200 metres and 400 metres, it will be remembered, are always reflected by this region during the daytime. It therefore seems probable that the maximum ionic density in E region is of the order 10^5 electrons per cubic centimetre.* By making observations with a range of wave-lengths round about 100 metres, it should be possible to find on any day what is the shortest wave-length deviated by E region. In this way it should be possible to compare the maximum ionic density in E region from day to day.

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* Observations made with 50-metre waves have shown that the upper F region has an electronic density at least four times this value.

It is of interest to examine if there is any evidence in published literature which supports or confirms the values given in this paper for the equivalent heights of the two ionized regions measured under comparable conditions of wave-length and distance between sending and receiving stations. Now Breit, Tuve and Dahl,* using the very elegant group-retardation method, have made many measurements of the equivalent height of the layer using 75 metre waves and working over a distance of 6 miles. Interpreting their results in terms of a single layer theory, they show that multiple reflections will explain their results in that the heights corresponding to successive reflections are approximately in the ratios 1 : 2 : 4. The three echoes received corresponded to layer heights at 105, 235 and 470 km. respectively.

Now the daytime equivalent heights of E and F regions, as measured in England with 100-metre waves, are about 100 km. and 230 km. respectively. We may therefore safely identify the value of 105 km. in America as corresponding to region E in England. But, in considering whether the remaining rays in the American experiments are multiply reflected rays from this region or not, we may note that, in terms of such an explanation, the triply reflected ray is missing, and the photographs published show that the doubly reflected ray is often of greater intensity than the singly reflected ray. Moreover, the heights are more nearly in the ratios 0·9 : 2 : 4 than in the ratios 1 : 2 : 4. All of these difficulties disappear if we adopt the double region hypothesis for the American results as well as for the English ones. According to this explanation the two regions in the Washington experiments had equivalent heights of 105 km. and 235 km. Singly-reflected rays were observed from both regions simultaneously, together with a doubly reflected ray from the upper region F. Such an interpretation is further supported by the fact that, in the majority of their recorded tests in the daytime, Breit, Tuve and Dahl got reflections corresponding to heights of 235 km. and 470 km., the reflection from the lower height of 105 km. being missing. This we should expect, since 70-metre waves require a greater electronic density to deflect them than do 100-metre waves; so that with the shorter waves reflection by E region should not be so frequent.

In comparing the results obtained at the three receiving stations at London, Cambridge and Peterborough, we again find that there is little difference between the equivalent heights recorded. It has, however, been found necessary to assume, in the case of the Peterborough results, that the interference takes place between singly reflected waves and doubly reflected waves from

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* 'Proc. Inst. Rad. Eng.,' vol. 16, No. 9, p. 1236 (September, 1928).

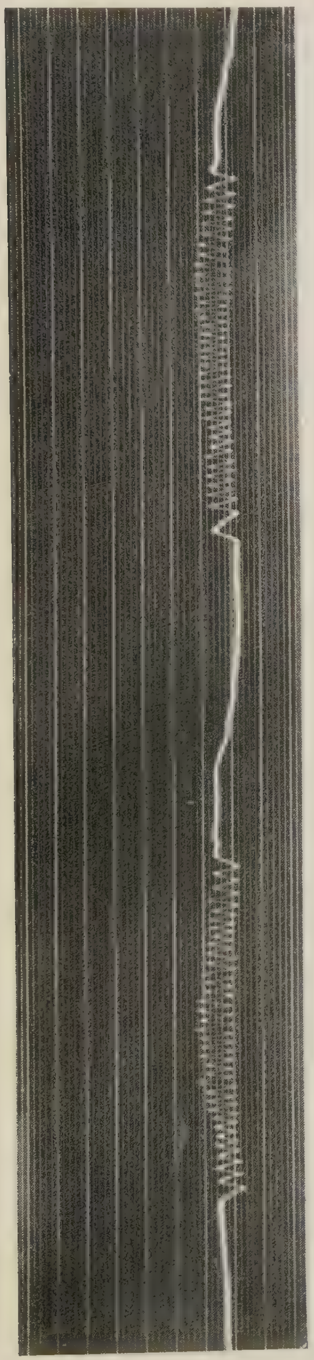


Fig. 5.

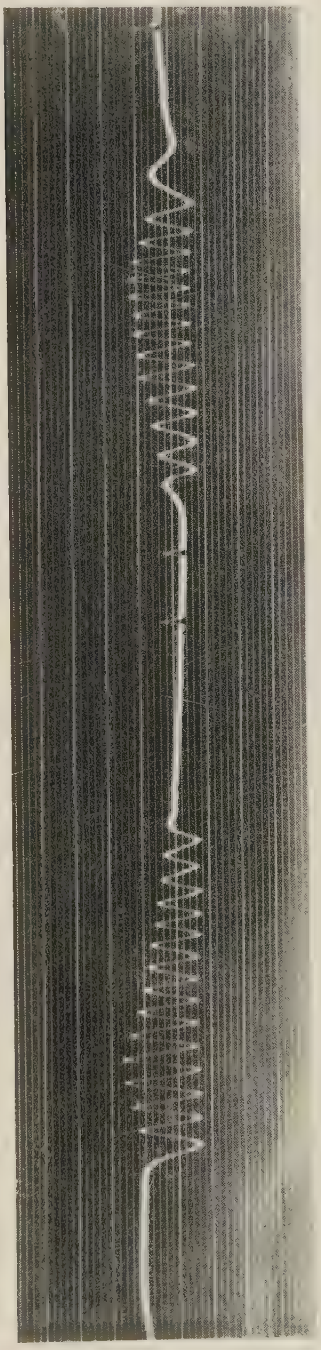
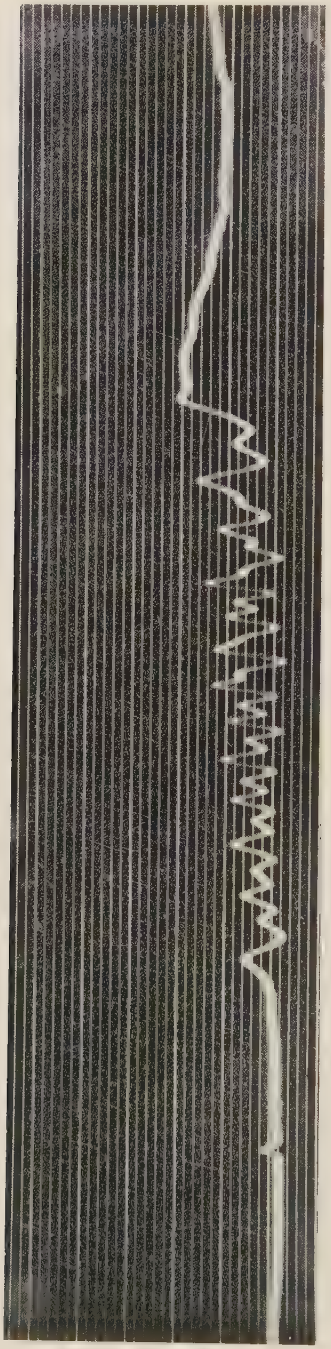


Fig. 6.

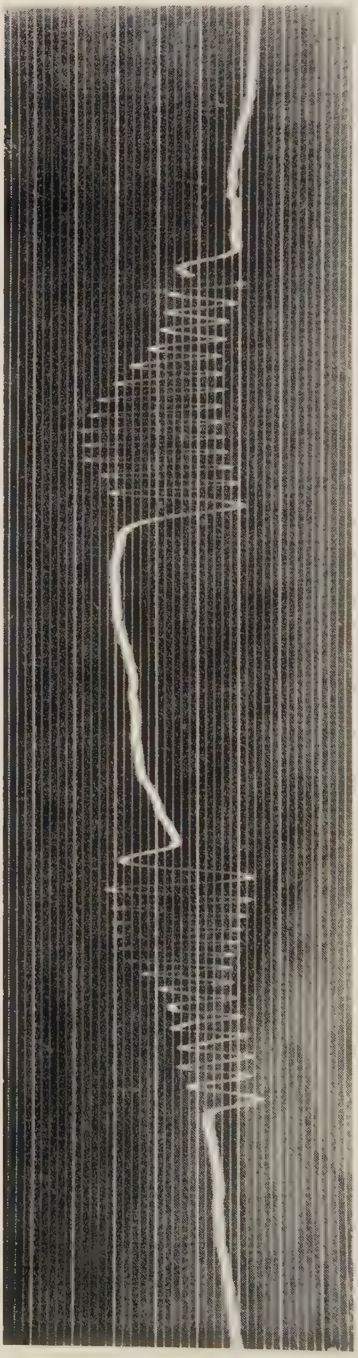
(*Facing p.* 176.)



| ← Frequency changing →

FIG. 7.

Signal intensity.



| ← Frequency changing → | | ← Frequency changing → |

FIG. 8.

Signal intensity.

the upper atmosphere, the former being responsible for the greater part of the signal and simulating the action of the ground waves in experiments on longer wave-lengths. To test whether this interpretation of the Peterborough results is the correct one for the case of 100 metres, an experiment was carried out in which the mean amplitudes of the signal as received on a loop aerial and also on a vertical-wire aerial were compared. The two aerial systems were adjusted by the inclusion of resistances, so that the signals received in them were equal when transmission took place along the ground from a local valve generator a few wave-lengths away. For two such aerial systems it is known* that the ratio of the mean signal in the loop system to the mean signal in the aerial system is equal to the cosecant of the angle of incidence of the received waves. In these experiments it was found that the mean signal in the loop receiver was about three times that in the vertical antenna receiver, proving that the angle of incidence of the waves at the ground was relatively small. This indicated that the mean intensity of the signal was due to downcoming waves.

Summary.

The results of a series of measurements of the equivalent heights of the ionized regions in the upper atmosphere are described and discussed. The measurements were made using 100-metre waves which were emitted by a sending station at Teddington and recorded at London, Cambridge and Peterborough. Evidence showing the existence of two deflecting regions was obtained, the equivalent heights of which were about 100 km. and 230 km. during the daytime. The lower region (E region) was found to reflect only in the daytime, and then usually only in the middle of the day. Agreement in the equivalent heights measured at the three stations was obtained by assuming that, at the near receiving station (King's College, London), interference between a downcoming ray and a ground ray took place, while at the most distant station (Peterborough) interference between a singly reflected ray and a doubly reflected wave produced the recorded signal maxima and minima. The equivalent height of the Kennelly-Heaviside layer (E region), in the early morning, is shown to be greater for 100-metre waves than for 400-metre waves.

Acknowledgments.

The experiments described above were carried out as part of the programme of the Radio Research Board of the Department of Scientific and Industrial Research. The authors wish to acknowledge their indebtedness to the many

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* 'Roy. Soc. Proc.,' A, vol. 109, p. 631 (1925).

collaborators who assisted in them; to Messrs. E. L. Hatcher and A. C. Haxton, who carried out the transmissions from the National Physical Laboratory on which all the observations were made; to Mr. J. A. Ratcliffe and Mr. Vedy, who made the whole of the Cambridge observations; to Mr. W. C. Brown and Mr. R. D. Gander for expert technical assistance at the Peterborough and London receiving stations respectively; and finally to Dr. D. Dye, F.R.S., who, by making far more accurate determinations of the frequency-changes employed than had previously been available, greatly increased the all-round accuracy of our measurements.

The Structure and Activation of the Phosgene Molecule. Part I.—*General Introduction—Predissociation of Molecules.*

By Victor Henri, Professor of Physical Chemistry at the University of Zürich, and Owen Rhys Howell, Lecturer at the College of Technology, University of Manchester.

(Communicated by T. M. Lowry, F.R.S.—Received November 14, 1929.—Revised March 31, 1930.)

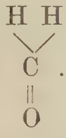
The study of diatomic molecules is already very advanced. By applying the principles of wave mechanics a number of authors, especially Hund, Heitler, London, Mulliken, Herzberg, Wigner and Witmer, have developed the theory of the conditions of formation, of electronic activation, and of different types of dissociation of diatomic molecules. They have also established relations between the electronic terms of atoms and those of related molecules, and have thus succeeded in arranging the terms of molecular spectra in a manner analogous to that for atomic spectra.

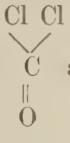
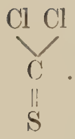
The experimental researches during recent years of Mulliken, Mecke, Hund, Diecke, Franck and his school, Hulthen, Birge, Hopfield, Richardson, Curtis, Johnson, Herzberg and many others have established a very exact knowledge of the structure of spectra of diatomic molecules.

The study of polyatomic molecules, however, is still in its infancy. Theory has not yet been developed and few complete experimental investigations have been made. The mathematician is in need of sufficient experimental basis for attacking theoretically the problem of the polyatomic molecule.

The study of triatomic molecules has been attempted; the ultra-violet absorption spectra of chlorine dioxide, sulphur dioxide and carbon disulphide having been measured by several observers. In this laboratory, the absorption spectrum of SO_2 and its analysis is being investigated by Motschan and that of CS_2 by Koffler. The interest of this simultaneous study is that these two molecules belong to entirely different types. Sulphur dioxide is a *triangular molecule* having a large electric moment of $\mu = 1 \cdot 61 \times 10^{-18}$ according to Zahn.* Carbon disulphide, on the other hand, has the same structure as CO_2; it is a *linear molecule* having a zero electric moment as found by Hoejendahl† from the experiments of Pohrt.‡ The same conclusion has been reached by Debye in his recent book§ and in a private communication.

The ultra-violet absorption spectra of other triatomic molecules have also been examined by different observers but the spectra are very complex and no complete analysis has been made.

Among tetra-atomic molecules, formaldehyde has been studied by Henri and Schou.|| This has been shown to be a Y-shaped molecule and may be written . The ultra-violet absorption spectrum of this compound consists of a series of vibration bands, each of which is composed of a large number of very fine lines which correspond to a double rotation state of the molecule.¶ The rotation lines are very sharp and easily measured, so that it has been possible to make a complete analysis of the rotation spectrum of this tetra-atomic molecule, and obtain the values of the moments of inertia.

Simultaneously, two other compounds of the same class of Y molecules have also been studied in this laboratory, namely, phosgene  and thiophosgene . These molecules have a structure quite analogous to that of formalde-

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* 'Phys. Rev.,' vol. 27, p. 455 (1926).

† 'Diss. Kopenhagen,' 1928.

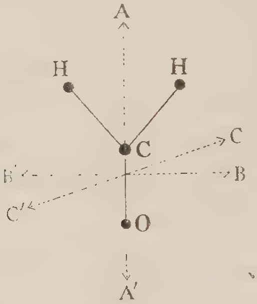
‡ 'Ann. Physik,' vol. 42, p. 569 (1913).

§ Debye, 'Polare Molekeln,' Leipzig, 1929.

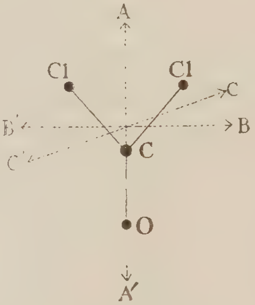
|| 'Z. Physik,' vol. 49, p. 774 (1928).

¶ Henri and Schou, 'Nature,' vol. 118, p. 225 (1926).

hyde, but they differ in possessing far greater moments of inertia. The rotation spectrum therefore consists of lines extremely close together, the distance between them being of the same order as the breadth of the lines themselves, so that it is impossible to measure them.



Formaldehyde.



Phosgene.

Formaldehyde possesses three moments of inertia: J about the axis AA′, K about the axis BB′, and L about the axis CC′. The third moment, L, is approximately equal to K. The values of these have been calculated from the rotation spectrum and found to be: $J_0 = 1\cdot38 \times 10^{-40}$; $K_0 = 23 \times 10^{-40}$. The distance between the hydrogen atoms is $1\cdot3 \times 10^{-8}$ cm. and between C and O $1\cdot2 \times 10^{-8}$ cm.

Phosgene also has three moments of inertia, but L is quite different from K. Since the atoms are all in one plane $J + K = L$.

The recent researches of Debye, Bewilogua and Ehrhardt,* on the scattering of X-rays by carbon tetra-chloride vapour, have established that the distance between neighbouring chlorine atoms in the molecule of carbon tetrachloride is $3\cdot1 \times 10^{-8}$ cm. Assuming that the chlorine atoms in the phosgene molecule are separated by the same distance, then the moment of inertia about AA′ is:

$$J = 2 \times 35 \times 1\cdot65 \times 10^{-24} \times (1\cdot55)^2 \times 10^{-16} = 266 \times 10^{-40},$$

and the other two moments of inertia, K and L, must be still greater.

The rotation spectrum (branches P and R) is approximately represented by the formula:

$$\frac{1}{\lambda} = \nu_0 \pm (B_0 + B')\,m + Cm^2$$

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* 'Phys. Zeit.,' vol. 30, p. 84 (1929).

where

$$B_0 = \frac{h}{8\pi^2 C}\left(\frac{1}{J_0} - \frac{1}{K_0}\right) = 27\cdot 7 \times 10^{-40}\left(\frac{1}{J_0} - \frac{1}{K_0}\right)$$

and

$$B' = \frac{h}{8\pi^2 C}\left(\frac{1}{J'} - \frac{1}{K_0}\right) = 27\cdot 7 \times 10^{-40}\left(\frac{1}{J'} - \frac{1}{K_0}\right).$$

Then, neglecting $\frac{1}{K_0}$ (since K_0 is very large)

$$B_0 + B' = \frac{2 \times 27\cdot 7 \times 10^{-40}}{266 \times 10^{-40}} = 0\cdot 2 \text{ cm.}^{-1}.$$

The spectrum due to the rotation about the axis AA′ is therefore composed, for each branch, of lines separated by less than 0·2 cm.$^{-1}$. The spectrum of the rotation about the axes BB′ and CC′ is composed of lines still more closely packed.

The breadth of the bands in the finest region of the absorption spectrum of phosgene is about 2 cm.$^{-1}$, so that in this small interval there are superposed more than 20 rotation lines. It is therefore evidently impossible to observe separately the rotation lines of a molecule-like phosgene. The superposition of the rotation lines produces a broadening of the vibration bands. Each band is degraded towards the visible and has a sharp edge towards the ultra-violet. This signifies that the moment of inertia is augmented by electronic activation of the molecule; in other words, the distance between the vibrating atoms increases. This can be very readily seen in fig. 1 which is a micro-

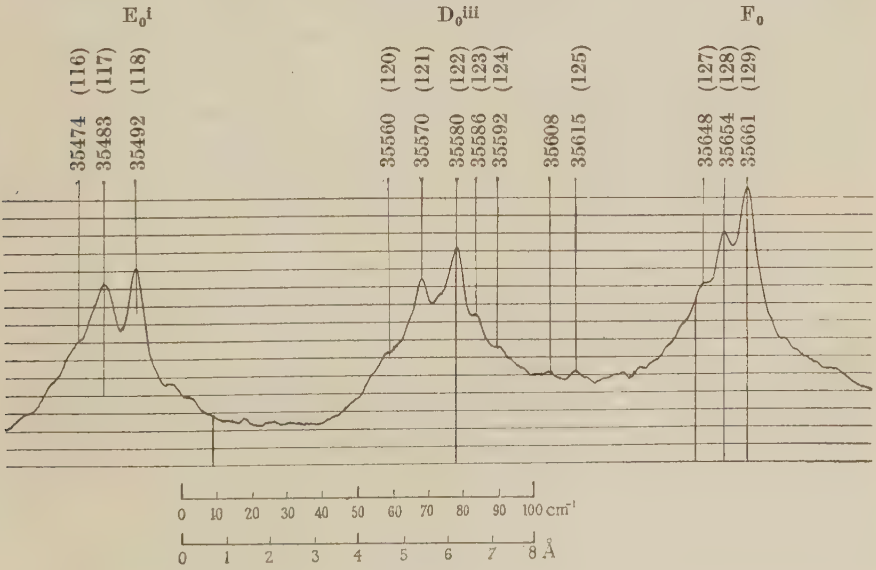

FIG. 1.

photogram of a small portion of the absorption spectrum of phosgene. This portion between $\lambda = 2820$ and 2800 Å. contains three groups of bands :—

No. 129 $\frac{1}{\lambda} = 35661$	No. 122 $\frac{1}{\lambda} = 35580$	No. 118 $\frac{1}{\lambda} = 35492$
,, 128 $\frac{1}{\lambda} = 35654$	,, 121 $\frac{1}{\lambda} = 35570$	,, 117 $\frac{1}{\lambda} = 35483$
,, 127 $\frac{1}{\lambda} = 35648$	,, 120 $\frac{1}{\lambda} = 35560$	,, 116 $\frac{1}{\lambda} = 35474$

The ultra-violet side falls more abruptly than the red side of each band. The rotation lines cannot be distinguished in this spectrum ; there must be more than 40 lines between the bands 129 and 128.

The absorption spectrum obtained with polyatomic molecules having large moments of inertia is therefore a pure vibration spectrum with a series of states of electronic activation, and its investigation involves an analysis of this vibration spectrum. The study of infra-red and of Raman spectra shows that all polyatomic molecules possess several fundamental frequencies of atomic vibration, which are designated α_0, β_0, γ_0, ..., for the normal molecule and α' β', γ', ..., for the activated molecule.

The entire spectrum is then represented by the formula :

$$\frac{1}{\lambda} = \nu_0 + p'\alpha'(1 - x'p') - p_0\alpha_0(1 - x_0p_0) + q'\beta'(1 - y'q') - q_0\beta_0(1 - y_0q_0) + \ldots,$$

where p_0, q_0 ... and p', q' ... are vibration quantum numbers for the normal and activated molecule respectively, and x, y, ... are correction factors for non-harmonicity of the vibrations. This formula is certainly incomplete. There must also be terms corresponding to the mutual influences of the different vibrations in the molecule, but there is not yet sufficient experimental data available for the determination of the form of these additional terms. We hope to obtain these terms by the accurate study of the vibration spectra of SO_2 and CS_2.

The coefficients x, y, ... are approximately inversely proportional to the moments of inertia of the molecule ; these moments are very large, consequently the collection for non-harmonicity in polyatomic molecules containing heavy atoms will generally be very small. This is true for phosgene, so that the formula for the vibration spectrum simplifies to

$$\nu = \nu_0 + p'\alpha' - p_0\alpha_0 + q'\beta' - q_0\beta_0 + \ldots.$$

which may also be written for convenience in calculation

$$\nu = \nu_0 + (p' - p_0)\alpha' + p_0(\alpha' - \alpha_0) + (q' - q_0)\beta' + q_0(\beta' - \beta_0) + \ldots.$$

The primary difficulty in the study of a vibration spectrum is to account for the observed bands in terms of this formula. In analysing such a spectrum, the problem consists in finding which vibration periods are due to the various atoms, both in the normal molecule and in the excited molecule.

The first important criterion in deciding whether certain intervals between the absorption-bands are due to the vibration in the normal molecule or in its excited state, is whether they occur in the direction of increasing or of decreasing wave-length. If a long series of intense bands occurs at regular intervals from a given origin towards the ultra-violet, this period may be ascribed with certainty to the atoms in the electronically excited molecule. If, on the other hand, a small number of bands of lower intensity is found distributed at regular intervals from each intense band towards the red, then these intervals are due to vibration periods of the atoms in the normal molecule.

The vibration periods of the atoms in the normal molecule can be also obtained from the infra-red vibration spectra. Unfortunately, these spectra have not been well elucidated and they cannot be measured with great precision since the bands are generally very broad. Very accurate measurements of infra-red absorption spectra have recently been made by Barnes.†

The same information can, however, be obtained from the Raman spectra, which gives the different vibration frequencies of the atoms in the normal molecule with great exactitude. Consequently the study of the ultra-violet absorption spectrum of a compound should always be made in conjunction with that of its Raman spectrum. This procedure has been adopted in this laboratory and has been applied with very satisfactory results to the study of the ultra-violet spectrum of chlorobenzene by Langseth,‡ of carbon disulphide by Koffler, of benzene and indene by Shapiro, and of benzaldehyde by Almasy. The present communication includes an account of the application of a knowledge of the Raman spectrum of phosgene to the elucidation of its ultra-violet absorption spectrum.

The study of the vibration spectrum gives important information regarding the structure of the molecule and the conditions of its stability.

For diatomic molecules Franck has shown that it is possible to calculate from the convergence of the vibration spectrum and from the values of the coefficients of non-harmonicity. x_0 and x', the energy of dissociation of a molecule AB into two normal atoms and also into activated atoms A* and B*.

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† 'Nature,' vol. 124, p. 300 (1929).

‡ 'Nature,' vol. 124, p. 92 (1929).

This method has been recently applied in the study of the molecule of sulphur monoxide SO.*

For polyatomic molecules, this criterion of the convergence of the vibration terms cannot be employed, or, rather, has not yet been applied. The stability of such molecules can, however, be deduced from a study of two characteristics of the spectra.

1. *Deformability.*—A frequency of vibration α_0 in the normal molecule becomes α' in the activated molecule. As a general rule α' is less than α_0 and this signifies that the distance between the vibrating masses is increased by electronic activation.

The binding force or the quasi-elastic force between the vibrating atoms is proportional to $\mu\alpha^2$, where μ is the electric movement of the molecule. Relative values of the " deformability " of molecules are given by the expression $(\alpha_0{}^2 - \alpha'^2)/\alpha^2$.

Kuhn† has shown from a study of the absorption spectra of chlorine, bromine and iodine that the value of $\mu\alpha_0{}^2$ is very exactly proportional to the heat of dissociation of Cl_2, Br_2 and I_2. The same result has been obtained by Rosen‡ for the molecules O_2, S_2, Se_2 and Te_2.

Another general relation has been found by Rosen and Mecke and extended by Henri between the vibration frequencies and the atomic numbers (Z_1, Z_2) of vibrating atoms in a diatomic molecule, namely, that the expression $\alpha_0{}^2Z_1Z_2$ is quite constant for a large number of different molecules. No similar relation has as yet been found for polyatomic molecules.

2. *Predissociation.*—It has been shown§ that, for a great number of substances, the vibration bands become diffuse at a certain wave-length and increase in breadth the further they occur towards the ultra-violet. This broadening of the vibration bands and disappearance of the quantisation of molecular rotation are accompanied by a number of changes in the properties of the molecule‖ :—

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* Henri and Wolff, ' J. Physique,' vol. 10, p. 81 (1929). This memoir also contains an historic account of vibration spectra and their relation to the different types of dissociation of molecules. See also Henri, " Structure des molécules et spectre de bandes." ' Réunion Internationale de Chimie Physique,' Paris, 1928.

† ' Z. Physik,' vol. 39, p. 77 (1926).

‡ ' Z. Physik,' vol. 43, p. 121 (1927).

§ Henri and Teves, ' Nature,' vol. 114, p. 894 (1924) ; Henri, ' Structure des molécules, Paris, 1925, p. 82 ; Henri and Schou, ' Z. Physik,' vol. 49, p. 818 (1928).

‖ For further details see Henri and Wurmser, ' J. Physique,' vol. 8, p. 289 (1927) ; Hemptine, ' J. Physique,' vol. 9, p. 357 (1928).

(*a*) The vibration frequency in this region becomes less, signifying an increase in the distance between the vibrating masses ; the molecule becomes *labile.*

(*b*) The fluorescence excited by the light in the region of the diffuse bands is very feeble or, indeed, entirely absent.

(*c*) The molecule becomes chemically active.

(*d*) The limiting wave-length at which these diffuse bands appear is displaced towards the red on raising the temperature, and the greater the molecular specific heat of the molecule, the greater the displacement. ("Thermal predissociation.")

Under the influence of light and also of heat, the molecule passes to a new state, intermediate between that of the normal molecule and the dissociated molecule, and this state has been given the name *predissociation* (Henri, *loc. cit.*).

Many authors (Kronig, Wentzel, Bonhoeffer, Rice, Franck, Sponer, Henri, etc.) have given a theory of the predissociation of molecules. The spectrum becomes diffuse because of a great diminution in the duration of life of the active molecule, which becomes of the same order of magnitude as the period of rotation. The great decrease in the life of the molecule occurs in general when, by the superposition of atomic vibration, the activated molecule acquires an energy level greater than that corresponding to the dissociation of the normal molecule into normal atoms, and also when the molecule, in a certain state of vibrational activation, can return to the initial state in two or more different ways ; this is a sort of Auger phenomenon.*

The experimental studies made in Zürich on the photochemical decomposition of benzaldehyde† and on acetaldehyde,‡ have demonstrated the remarkable agreement between the energy of dissociation of the molecule and the wave-length at which the spectrum begins to become diffuse.

The primary photochemical reactions are

$$C_6H_5CHO + h\nu \rightarrow C_6H_5 + CO + H$$
$$CH_3CHO + h\nu \rightarrow CH_3 + CO + H.$$

The corresponding energies calculated from thermochemical data are—155780 and — 93300 cals. respectively. These energies correspond to the wave-lengths λ = 2461 Å. and 3050 Å., whilst the region of predissociation is found to begin at room temperature with benzaldehyde at λ = 2460 Å. and with acetaldehyde at λ = 3054 Å.

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* Bonhoeffer, 'Z. Phys. Chem.,' vol. 134, p. 337 (1929) ; Franck and Sponer, "Göttingen Nachr.," 1929.

† de Hemptine, 'J. Physique,' vol. 9, p. 356 (1928).

‡ Smith, appearing in 'Z. Phys. Chem.,' 1930.

Similarly, good agreement is found for sulphur vapour. S_2 gives an absorption spectrum composed of very fine lines which become diffuse abruptly at λ = 2792 Å. The energy of dissociation of $S_2 = 2S$ at 400°–600° is 103,500 cals.* which corresponds to λ = 2760 Å. The determination of the energy of dissociation is not very accurate; the agreement between the observed and calculated limits of predissociation is therefore satisfactory.

Benzaldehyde vapour (de Hemptine) and acetaldehyde vapour (Smith) at room temperature undergo no photochemical decomposition with light of λ = 2750 and 3050 Å. respectively, and the absorption bands at these wave-lengths are sharp; at 200°, however, photochemical decomposition does occur and the absorption bands become broad and diffuse in these regions.

Diffuse absorption bands are therefore characteristic of a special chemical sensitivity of the molecule. Consequently, it is possible by determining the limiting wave-length at which the bands in the absorption spectrum begin to become diffuse, to predict that photochemical action on the molecules will begin only with light of shorter wave-length and to calculate the energy of primary dissociation of the molecule.

The study of phosgene is of general interest, because the molecule contains a carbonyl group, CO. The absorption spectra of different molecules containing a CO group have been studied in this laboratory by Lardy, Grossmann, Light, Luthy, Almasy, de Hemptine, Schou and Henri; the absorption spectrum of carbon-monoxide itself has also been studied (Henri and Schou, 'C.R.,' Paris).

The presence of the carbonyl group in a molecule always produces an absorption band in the middle of the ultra-violet (between 3200 and 2600 Å.). If the compound is in the vapour state, the spectrum is composed of a large number of fine bands distributed at regular intervals. Towards the ultra-violet these bands become broad and diffuse, at a certain point, corresponding to a predissociation of the molecule.

All these molecules undergo photochemical and thermal decomposition, with production of carbon monoxide, hydrocarbons and hydrogen. For phosgene, the same decomposition gives CO and chlorine.

The exact mechanism of the separation of CO from the rest of the molecule is as yet not fully explained. The carbon atom in carbon monoxide is probably in a different electronic state from that of the carbon atom in molecules like aldehydes, ketones or phosgene. In carbon monoxide, it is very probable (Johnson) that the carbon atom is in its normal state, that is a ^3P state, but in a molecule like phosgene, the carbon atom is tetravalent and is in the activated state ^5S. The same must be true of the carbon atom in aldehydes and ketones, so that the carbonyl group in all these molecules is different in its electronic configuration from carbon monoxide itself.

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* Budde, 'Z. Anorg. Chem.,' vol. 79, p. 169 (1912).

Confirmation of this conclusion is found in the measurements of the polarity of carbon monoxide and of molecules containing the carbonyl group. The electric moment of carbon monoxide is $\mu = 0 \cdot 10 \times 10^{-18}$ *; that of several ketones is $\mu = 2 \cdot 7 \times 10^{-18}$,† the influence of substitution being very small (thus for $CH_3 . CO . CH_3$ $\mu = 2 \cdot 71$ and for C_3H_7 $\mu = 2 \cdot 73$). The large value of the polarity of ketones and aldehydes is determined by the carbonyl group; this high value of μ must therefore be explained by the difference in the distribution of electrons in the carbon atom of carbonyl and of carbon monoxide.

The comparative study of the vibrational frequencies of different types of molecules containing the carbonyl group will give important results concerning the mutual influence of atoms in the molecule. A comparison of the different carbonyl compounds is given later.

A further point of general interest which arises from a study of the absorption spectrum of phosgene is the possibility of determining the isotope effect for polyatomic molecules. Mulliken‡ and later Mecke and many other observers, especially Birge, Elliott and Curtis, have obtained a rotational and vibrational isotope effect for many different diatomic molecules. For the chlorine molecule, Elliott§ has measured the vibrational isotope effect corresponding to the molecules $Cl^{35}Cl^{35}$, $Cl^{35}Cl^{37}$ and $Cl^{37}Cl^{37}$. He observed that the separation corresponding to the first two isotopes is equal to $9 \cdot 6 \pm 0 \cdot 2$ cm.$^{-1}$ for the band $\nu_0 = 19389$ cm.$^{-1}$.

If the vibrational energy is represented by $E_p = h\alpha cp\,(1 - xp)$, then the separation for the two isotopes is :—

$$\nu_1 - \nu_2 = (1 - \rho)\,(\alpha' p' - \alpha_0 p_0) - (1 - \rho^2)\,(\alpha' x' p'^2 - \alpha_0 x_0 p_0{}^2),$$

where

$$\rho^2 = \frac{\mu_1}{\mu_2} = \frac{m' + m_2}{m' + m_1}\,\frac{m_1}{m_2},$$

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* Zahn and Miles, 'Phys. Rev.,' vol. 32, p. 497 (1928).

† Wolf, 'Z. Phys. Chem.,' B, vol. 2, p. 39 (1929).

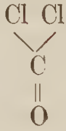
‡ 'Phys. Rev.,' vol. 25, p. 119, and vol. 26, pp. 1, 319 (1925).

§ 'Roy. Soc. Proc.,' vol. 123, p. 629 (1929).

m' being the mass of A and m_1 and m_2 the masses of B_1 and B_2 respectively in the molecules AB_1 and AB_2.

By assuming for the chlorine molecule $\alpha_0 = 565$ cm.$^{-1}$ and $\alpha' = 120$ cm.$^{-1}$, $p_0 = 2$ and $p' = 18$, Elliott obtained a value for the separation of isotopes very closely equal to the observed.

The theory of the isotope effect has recently been developed by Curtis and Patkowski* from a very accurate experimental study of the absorption spectrum of iodine monochloride. The separation between the bands of ICl^{35} and ICl^{37} increases for the first successive values of the vibration quantum numbers of the activated molecule, then attains a maximum and falls for higher values of vibration quanta.

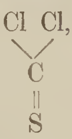
This theory cannot be directly extended to polyatomic molecules. The frequency of vibration in these molecules is not dependent on the masses of only two atoms, but is influenced by those of the other atoms; and the different fundamental vibrations in the molecule are not independent, but are mutually influenced by those of all the other atoms. The theoretical treatment of the isotope effect in polyatomic molecules cannot be developed, because there is no available data on the laws of the mutual influence of the different atoms in the molecule. We can only assume that the separations due to the isotope effect will be greater for certain vibrations than for others. For example, in the molecule of phosgene  $\mathrm{Cl_2C{=}O}$, it may be supposed that there are three fundamental frequencies corresponding to vibrations between (1) Cl and Cl; (2) Cl and C; and (3) C and O. If these vibrations were totally independent, we should observe triplets for the bands corresponding to (1), doublets for the bands corresponding to (2) and singlets for the bands corresponding to (3), and the separations should be different for (1) and (2). These three sorts of bands are actually found in the absorption spectrum. Thus, for example, in the microphotogram (fig. 1) of a portion of the phosgene spectrum, can be seen very clearly the triplet No. 129, 128, 127 with separations 35661 — 35654 = 7 cm.$^{-1}$ and 35654 — 35647 = 7 cm.$^{-1}$; band No. 122 shows a well-developed doublet with separation 35580 — 35570 = 10 cm.$^{-1}$, and there is indication of a third band 35560. The same appearance is presented by band No. 118, which is a doublet 35492 — 35483 = 9 cm.$^{-1}$, with indication of a third component 35474.

* 'Faraday Trans.,' vol. 25, p. 725 (1929).

The relative intensities of the components of these triplets correspond quite well with the abundance of the different isotope molecules. The variation of the separation between the isotopic bands for successive quantum numbers is, however, not so simple as in diatomic molecules; it is therefore not possible as yet to calculate from these separations the absolute values of the vibration quanta, but it may be observed that the separation increases from the red to the ultra-violet end of the spectrum.

An analogous isotope effect for polyatomic molecules was recently observed in the absorption spectrum of chlorine dioxide by Goodeve and Stein.* The separation does not seem to be the same as for a simple diatomic molecule. It is therefore of great interest to study the isotope effect for different sorts of polyatomic molecules.

In this laboratory, Langseth† has observed a doubling of certain bands with chlorobenzene which is probably due to the isotope effect produced by the chlorine atom.

A similar isotope effect to that of phosgene is shown in the absorption spectrum of thiophosgene , which we have studied. This spectrum will be published in a further paper.

* 'Faraday Trans.,' vol. 25, p. 738 (1929).

† 'Nature,' vol. 124, p. 92 (1929).

The Structure and Activation of the Phosgene Molecule.
Part II.—*The Raman Spectrum of Phosgene.*

By Victor Henri, Professor of Physical Chemistry at the University of Zürich, and Owen Rhys Howell, Lecturer at the College of Technology, University of Manchester.

(Communicated by T. M. Lowry, F.R.S.—Received November 14, 1929.)

The vessel in which the phosgene was contained for illumination was a glass tube 3 cm. diameter and 10 cm. long, closed at one end and ending at the other in a " tail " bent at right angles. The tail had a bulb of about 25 c.c. capacity to allow for subsequent expansion of the liquid after filling at low temperature, and it was coated with black wax to prevent reflection from this end of the vessel.

This Raman tube was filled in the following way. A stream of phosgene from a bomb (supplied by Messrs. Siegfried, of Zofingen) was led through a glass coil cooled in a freezing mixture of ice and salt. The condensed phosgene was received in a bulb of about 120 c.c. capacity cooled in ether and carbon dioxide ice. The bulb was joined to the Raman tube and a side tube was provided for evacuation. When a sufficient quantity of liquid had been collected, the receiving bulb was sealed off from the condenser coil, the two bulbs were evacuated through calcium chloride tubes by means of a water-pump and the side tube was sealed off. The Raman tube was then cooled in alcohol and carbon dioxide ice and the receiving bulb allowed to warm slowly, so that the phosgene distilled over quietly without ebullition. When the requisite amount was present, the tube was sealed off. The liquid produced in the initial condensation was somewhat cloudy but on redistillation into the Raman tube it was obtained perfectly clear.

The method of obtaining the spectrum was as follows. A wooden box (35 × 15 × 20 cm.) was provided with two glass windows; one (7 × 3 cm.) at one side and the other (3 cm. diameter) in front. The Raman tube was suspended in the box parallel to the rectangular window and in line with the circular one. The tube was illuminated through the side window by a mercury-vapour lamp. Pieces of highly polished aluminium foil were bent round the lamp to the window and round the tube to the window to serve as reflectors and so secure as great a concentration of light as possible in the tube. A stream of cold water was kept flowing through the box and a jet of dry air was directed against the circular window to prevent deposition of moisture.

The emergent light was focussed by two lenses on to a spectrograph and an exposure of 26 hours was made. Details of the spectrum are given in Table I.

Table I.—Raman Spectrum of Phosgene.

Intensity.	$\frac{1}{\lambda}$	$\Delta \frac{1}{\lambda}$ from the Hg line :—	
		$\lambda = 4358 \cdot 6$ A. $\frac{1}{\lambda} = 22937$ cm.$^{-1}$.	$\lambda = 4046 \cdot 9$ A. $\frac{1}{\lambda} = 24703$ cm.$^{-1}$.
	cm.$^{-1}$.	cm.$^{-1}$.	cm.$^{-1}$.
3	22370	567	—
1	22494	443	—
2	22648	289	—
3	24137	—	566
1	24259	—	444
2	24412	—	291

Mean values : $a = 567 \pm 8$ cm.$^{-1}$. $b = 443$. $c = 290$.

There are therefore three vibration frequencies corresponding to wave-lengths 17·6, 22·5 and 34·4 μ. The infra-red absorption spectrum has not been measured for long wave-lengths, so that it is not possible to compare the Raman spectrum with it.

The Structure and Activation of the Phosgene Molecule. Part III.—*A Study of the Ultra-Violet Absorption Spectrum of Phosgene Vapour.*

By Victor Henri, Professor of Physical Chemistry at the University of Zürich, and Owen Rhys Howell, Lecturer at the College of Technology, University of Manchester.

(Communicated by T. M. Lowry, F.R.S.—Received November 14, 1929—Revised March 31, 1930.)

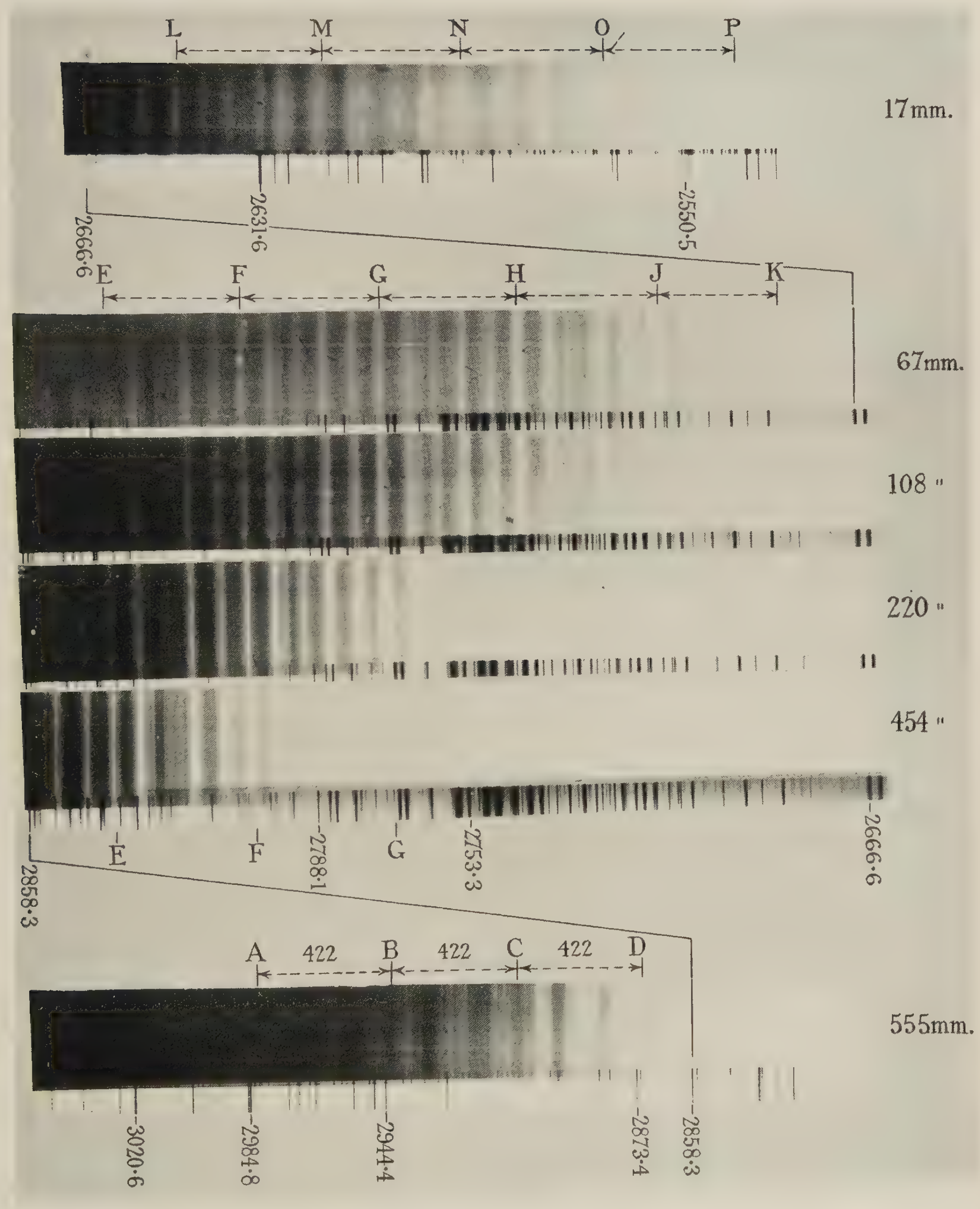
[Plates 4, 5.]

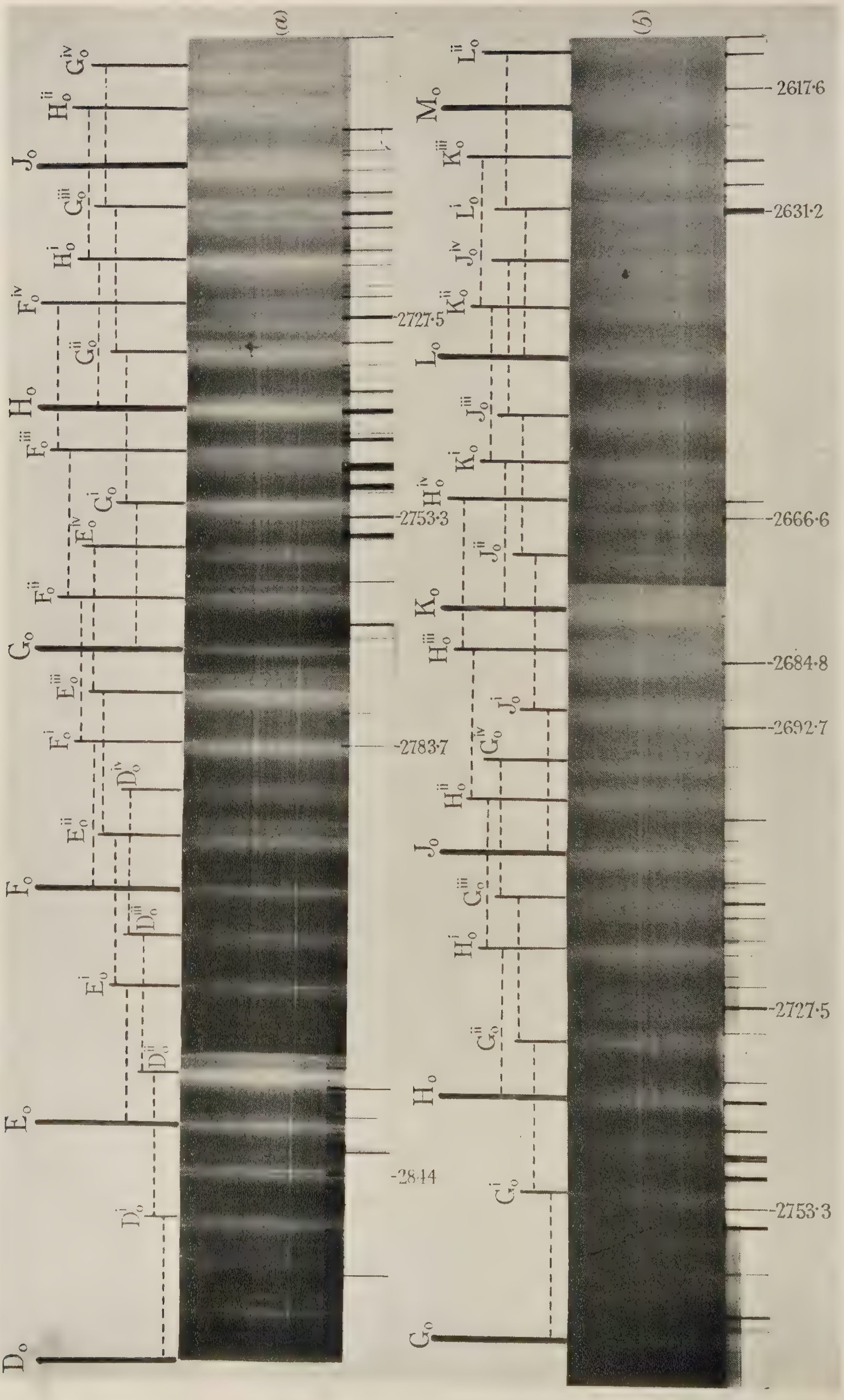
1. *Experimental.*

The phosgene used was Kahlbaum's purest and was first fractionally distilled. Two double-necked bulbs, each of about 50 c.c. capacity, were sealed together with a tap between. The free limb of the second bulb was also provided with a tap and connected to two Langmuir pumps in series. The phosgene was cooled in solid carbon dioxide and ether and about 10 c.c. was transferred to the first bulb which was similarly cooled and which was then sealed off. The second bulb was evacuated, put in connection with the first bulb until full of vapour and then evacuated again. This was repeated several times until about 2 or 3 c.c. of phosgene had disappeared. The second bulb was then cooled with solid carbon dioxide and ether and the first bulb allowed to warm slowly until about a third of the phosgene remaining had distilled over. The second bulb was then sealed off from the first and was connected at D to the absorption apparatus shown in fig. 2.

The absorption tube itself consists of a glass tube TT fitted by means of ground joints with two end pieces EE for convenience in cleaning. The total length is 100 cm. The end pieces are provided with polished quartz windows QQ fitted on with cement. The tube is in connection with two bulbs ; a small one S of about 20 c.c. capacity and a large one L of about 500 c.c. These bulbs are connected to one another and to a mercury manometer M by which the pressure in the tube may be registered. The storage bulb G is attached by means of a mercury sealed joint J.

The method of manipulation is as follows. With tap *g* closed, the whole apparatus is evacuated through V by means of two Langmuir pumps in series, a vacuum of less than 1/1000 mm. being thus obtained. The tap *h* is then


L
M
N
O
P
17mm.
2631·6
2550·5
2666·6
E
F
G
H
J
K
67mm.
108 "
220 "
454 "
2666·6
E
F
2788·1
G
2753·3
2858·3
A
422
B
422
C
422
D
555mm.
3020·6
2984·8
2944·4
2873·4
2858·3


(a)
(b)
G_o^{iv}
H_o^{ii}
J_o
G_o^{iii}
H_o^{i}
F_o^{iv}
G_o^{ii}
H_o
F_o^{iii}
G_o^{i}
E_o^{iv}
F_o^{ii}
G_o
E_o^{iii}
F_o^{i}
D_o^{iv}
E_o^{ii}
F_o
D_o^{iii}
E_o^{i}
D_o^{ii}
E_o
D_o^{i}
D_o
-2727·5
-2753·3
-2783·7
-2844
L_o^{ii}
M_o
K_o^{iii}
L_o^{i}
J_o^{iv}
K_o^{ii}
L_o
J_o^{iii}
K_o^{i}
H_o^{iv}
J_o^{ii}
K_o
H_o^{iii}
J_o^{i}
G_o^{iv}
H_o^{ii}
J_o
G_o^{iii}
H_o^{i}
G_o^{ii}
H_o
G_o^{i}
G_o
-2617·6
-2631·2
-2666·6
-2684·8
-2692·7
-2727·5
-2753·3

closed and *g* opened, whereby the reservoir G is filled with vapour from the phosgene bulb. This is repeated several times and then a few cubic centimetres of liquid are distilled over into G by immersing it in a freezing mixture. Taps *g* and *h* are closed and the rest of the apparatus is again thoroughly evacuated. Any desired quantity of vapour can then be admitted into the absorption tube by opening G to S, then S to L, and finally L to the tube.

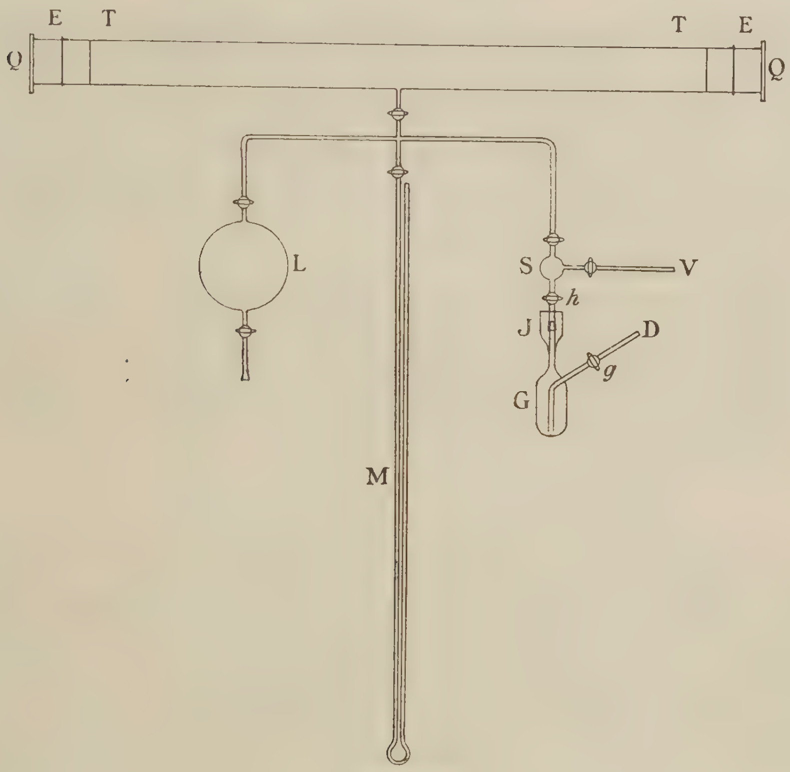


Fig. 2.

Exposures are first made with a very small pressure of vapour and then with a series of increasing pressures. The pressures employed for phosgene varied from 0·1 up to 680 mm. of mercury.

The source of ultra-violet light was a strong high-frequency spark between copper or aluminium electrodes under water, details of which have already been published.*

The comparison spectrum was from a condensed iron spark with self induction as recommended by Hemsalech, which gives very fine lines. The spectra were photographed on a Hilger E_1 spectrograph. The time of exposure was about 10 minutes for the absorption spectra and 10 to 30 seconds for the iron spectra.

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* Henri and de Làszlò, ' Roy. Soc. Proc.,' A, vol. 105, p. 662 (1924).

The absorption spectra were measured directly on the plates by means of a Jobin comparator and also with a Zeiss microscope micrometer attachment. They were also measured with a rule on photographic enlargements made with a very accurately corrected objective. The measurements by these three methods agreed to within one wave number. The wave-lengths are expressed in international Ångström units in air and the wave-numbers are reduced to vacuo and expressed in $cm.^{-1}$.

Accurate measurements of intensities and of separations between certain lines have also been made by microphotometric registration of the spectrum with the Moll's microphotometer of Kipp and Zonen (model 1929). Some of these photomicrograms are reproduced in figs. 1 (p. 181), 3 and 4 (p. 196).

2. *General Description of the Absorption Spectrum.*

The absorption spectrum of phosgene is composed of about 270 bands distributed between 3050 and 2380 A. These bands are not all present at the same time. At low pressures of 1 or 2 mm., only those bands in the extreme ultra-violet between 2500 and 2380 A. make their appearance. Beyond 2380 A. the absorption is continuous and becomes increasingly great towards the region of shorter wave-length. At a pressure of 4 mm. a whole series of bands appear between 2850 and 2600 A., those on the ultra-violet side being stronger than those on the red. As the pressure is further increased, the bands become stronger and stronger; those towards the ultra-violet fuse together while new bands make their appearance towards the red. This continues until at 680 mm. bands are obtained between 3050 and 2380 A. Beyond 2380 A. absorption is complete.

The change in the extent of the absorption with pressure is illustrated in Table II. Column 1 gives the pressure of vapour with a thickness of 100 cm.; column 2 indicates the molecular concentration of vapour calculated from the formula $C = p/22 \cdot 4 \times 760$; column 3 shows the value of 1/100 C, which is a measure of the increase of the intensity of absorption; column 4 gives the limits within which bands appear and the approximate position of the bands; column 5 shows the region beyond which complete absorption begins.

The absorption spectrum of phosgene has a very characteristic appearance shown in the photographic reproduction in Plate 4. Enlargements of a portion

Table II.

Pressure. mm.	Molecular concentration $c = p/22{\cdot}4 \times 760$.	Intensity of absorption. 1/100 C.	Bands present.	General absorption from λ
0·1	$0{\cdot}06 \times 10^{-4}$	—	None	—
0·3	0·18	—	None	—
0·6	0·35	—	None	—
1·4	0·82	122	M to R	<2349
4	2·35	42	E ,, U	2380
8	4·70	21	E ,, Q	2520
17	9·99	10	E ,, O	2550
25	14·69	6·8	E ,, L	2615
48	28·20	3·6	D ,, K	2680
67	39·36	2·6	D ,, K	2680
83	48·75	2·04	D ,, J	2700
125	73·43	1·37	C ,, H	2720
166	97·51	1·03	C ,, H	2730
375	220·2	0·45	B ,, F	2820
555	326·0	0·30	A ,, E	2850
680	399·5	0·25	A ,, D	2880

of this spectrum: (*a*) from $\lambda = 2863$ to 2693 A., and (*b*) from $\lambda = 2770$ to 2614 A., are given in Plate 5.

The spectrum is composed of a large number of intense doublets, and sometimes triplets, distributed at approximately regular intervals of about 9 to 12 A. Between these doublets are many fainter lines irregularly distributed. The microphotogram (fig. 1) shows the structure of a portion of the spectrum, the corresponding bands being indicated in Plate 5 (*a*).

The separation of these doublets in the region of 2800 A. (fig. 1) is about 0·8 to 1·0 A.

The bands of which the doublets are composed are fairly fine and their positions can be determined to within one or perhaps two wave-numbers. They have a sharp edge on the ultra-violet side and are degraded towards the visible side (fig. 1). At wave-lengths less than 2750 A. the bands become less sharp; they grow broader and the edges become more indefinite and diffuse. The further they occur in the ultra-violet, the more diffuse are the bands, and beyond 2650 A. it is impossible to distinguish the doublets. The bands are then about 1 to 2 A. broad, and beyond 2550 A. they exceed 3 A. in breadth. Although they are diffuse, their distribution remains regular.

This broadening is clearly visible in the photographic reproduction (Plate 5 (*b*)) and also in figs. 3 and 4, which are photomicrograms of the sharp doublets No. 151, 152 ($1/\lambda = 36073$ and 36082, Band G_0) and (on the same scale) of the diffuse band No. 230 ($1/\lambda = 37665$). In fig. 4, the irregularities are due to the grains of the photographic plate.

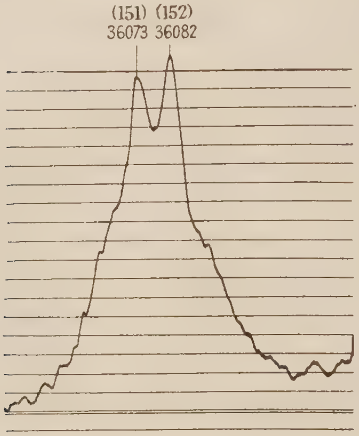

Fig. 3.

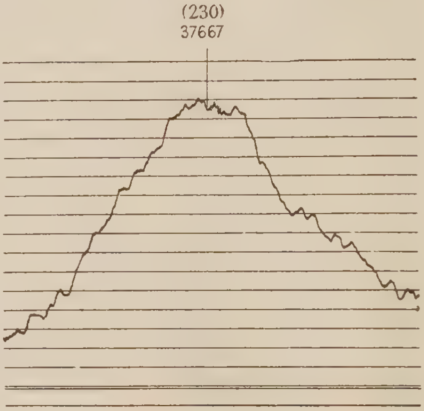

Fig. 4.

4. *Analysis of the Absorption Spectrum.*

The absorption spectrum is composed of a series of groups of bands distributed at regular intervals. Each of these groups is composed of six or seven intense doublets and a number of isolated lines. The groups are almost identically superposable, the period being about 422 cm.$^{-1}$. The spectrum may thus be divided into 11 or 12 successive groups, and these are designated by the letters A_0, B_0, C_0, etc., beginning at the red end. The interval between corresponding bands in each of these groups is constant at 422 cm.$^{-1}$ for the first seven groups, but it decreases in the region where the bands begin to become diffuse (region of predissociation).

There is therefore a principal fundamental vibration period of 422 corresponding to certain atomic vibrations in the phosgene molecule.

Table III gives the positions of the intense bands which have been chosen as origins for the different groups and also the intervals between the origins.

Since the groups are arranged at intervals of 422 cm.$^{-1}$ from the visible towards the ultra-violet, it follows that this interval is due to a vibration period in the activated molecule. This period is designated $\alpha' = 422$ cm.$^{-1}$.

It is then found that from the head of each group, four or five strong bands occur at a constant interval of 254 cm.$^{-1}$ towards the ultra-violet. This interval must, therefore, also be due to a vibration period in the activated molecule. It is designated $\beta' = 254$ cm.$^{-1}$.

Table III.

Group origins.	p'.	λ (air).	1/λ (vac.).	Interval.
		A.	cm.⁻¹.	cm.⁻¹.
A_0	0	2979·7	33551	
B_0	1	2942·7	33973	422
C_0	2	2906·5	34395	422
D_0	3	2871·3	34817	422
E_0	4	2836·9	36239	422
F_0	5	2803·4	35661	422
G_0	6	2770·6	36082	421
H_0	7	2739·1	36498	416
J_0	8	2708·5	36910	412
K_0	9	2678·4	37325	415
L_0	10	2648·1	37751	426

The corresponding bands are designated A_0^{i}, A_0^{ii}, A_0^{iii}, A_0^{iv}, B_0^{i}, B_0^{ii} .... These bands are marked on the photograph, Plate 5. Table IV contains the observed wave-numbers and the corresponding differences. The mean value is 254 cm.⁻¹.

Table IV.

A_0	—		A^{i}	—		A^{ii}	34056		A^{iii}	—			A^{iv}	34567
									511 = 2 ×		*255*			
B_0	—		B^{i}	34227	*253*	B^{ii}	34480	*260*	B^{iii}	34740	*248*		B^{iv}	34988
C_0	34395	*254*	C^{i}	34649	*253*	C^{ii}	34902	*255*	C^{iii}	35157	*256*		C^{iv}	35413
D_0	34817	*255*	D^{i}	35072	*251*	D^{ii}	35323	*257*	D^{iii}	35580	*253*		D^{iv}	35833
E_0	35239	*253*	E^{i}	35492	*256*	E^{ii}	35748	*253*	E^{iii}	36001	*256*		E^{iv}	36257
F_0	35661	*254*	F^{i}	35915	*254*	F^{ii}	36169	*255*	F^{iii}	36424	*255*		F^{iv}	36679
G_0	36082	*252*	G^{i}	36334	*258*	G^{ii}	36592	*254*	G^{iii}	36846	*256*		G^{iv}	37092
H_0	36498	*255*	H^{i}	36753	*252*	H^{ii}	37005	*255*	H^{iii}	37260			H^{iv}	—
J_0	36910	*255*	J^{i}	37165	*248*	J^{ii}	37413	*252*	J^{iii}	37665			J^{iv}	—

Similarly, from each group head, but now towards the red, there is a series of two or three fainter lines at a constant interval of 302 cm.⁻¹. This interval is therefore due to a vibration period in the normal molecule, and as it corresponds to β′ it is designated $\beta_0 = 302$ cm.⁻¹.

It was difficult to find the vibration frequency α_0 in the normal molecule corresponding to α′ in the activated molecule, but the study of the Raman spectrum proved of great assistance in deciding its value.

Since the bands are all degraded towards the visible, the frequency α_0 must be higher than $\alpha' = 422$. The Raman spectrum contains two lines, $a = 567$, and $c = 290$ cm.$^{-1}$. The accuracy of these measurements is not very high and it is therefore probable that a is a harmonic of c. The expected value of α_0 is therefore equal to or slightly greater than that of a or $2c$. Now there are two or sometimes three bands towards the red from each origin A_0, B_0, C_0, ... at a constant interval equal to 582 cm.$^{-1}$. We therefore accept this frequency as the value of α_0.

The absorption spectrum of phosgene is therefore characterised by two pairs of vibration periods: 582 and 302 cm.$^{-1}$ for the normal molecule and 422 and 254 cm.$^{-1}$ for the activated molecule.

From the analysis of the spectrum it follows that the normal molecule of phosgene has three energy levels separated by intervals of 592 cm.$^{-1}$. The bands A_0, B_0, C_0, ... are the strongest. From these origins, there are two bands towards the red at the distance equal to 582 cm.$^{-1}$, but there are no bands at the same interval towards the ultra-violet. It follows that the majority of the molecules are in the zero state ($p_0 = 0$ or possibly $\frac{1}{2}$) and the other vibration states of the normal molecule correspond to $p_0 = 1$ and 2 (or $1\frac{1}{2}$ and $2\frac{1}{2}$).

In conjunction with each of the vibration states of frequency α_0 are those of frequency $\beta_0 = 302$ cm.$^{-1}$. There are three such levels and the corresponding quantum states are denoted by $q_0 = 1$, 2 and 3. The bands are most intense for $q_0 = 1$, feebler and often non-existent for $q_0 = 2$ and 3.

The activated molecule possesses two vibration periods whose quantum numbers are denoted by p' and q'. p' possesses all the values from 0 to 11 and q' from 0 to 6.

When p' is not greater than 6, the corresponding bands are fine with sharp edges. When $p' = 7$ (group H; $\lambda = 2740$) the bands begin to become diffuse and their positions cannot be determined with an accuracy greater than 3 cm.$^{-1}$. With p' greater than 7, the bands get more and more diffuse until for $p' = 11$ (group M; $\lambda = 2615$) the width of the band is about 26 to 30 cm.$^{-1}$, and it is impossible to indicate the exact position of the head of the group (Plate 5 (*b*) and fig. 4).

The general structure of the absorption spectrum of phosgene can be illustrated by the schematic representation shown in fig. 5.

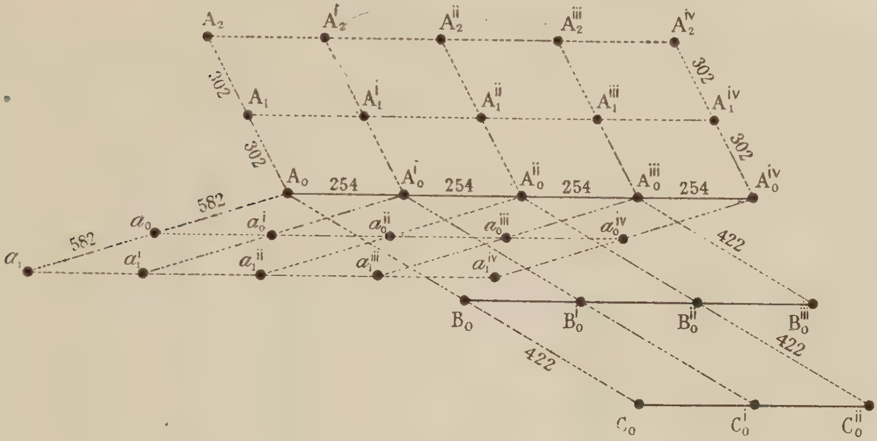
A₂
A₂ⁱ
A₂ⁱⁱ
A₂ⁱⁱⁱ
A₂ⁱᵛ
302
A₁
A₁ⁱ
A₁ⁱⁱ
A₁ⁱⁱⁱ
A₁ⁱᵛ
302
302
302
A₀
254
A₀ⁱ
254
A₀ⁱⁱ
254
A₀ⁱⁱⁱ
254
A₀ⁱᵛ
582
582
a₀
a₀ⁱ
a₀ⁱⁱ
a₀ⁱⁱⁱ
a₀ⁱᵛ
a₁
a₁ⁱ
a₁ⁱⁱ
a₁ⁱⁱⁱ
a₁ⁱᵛ
422
B₀
B₀ⁱ
B₀ⁱⁱ
B₀ⁱⁱⁱ
422
422
C₀
C₀ⁱ
C₀ⁱⁱ

Fig. 5.

The general formula representing the whole band system is :—

$$1/\lambda = 33551 + 422p' - 582p_0 + 254q' - 302q_0$$

or

$$1/\lambda = 33655 + 422\,(p' + \tfrac{1}{2}) - 582\,(p_0 + \tfrac{1}{2}) + 254\,(q' + \tfrac{1}{2}) - 302\,(q_0 + \tfrac{1}{2}).$$

This formula may be written for easier calculation :

$$1/\lambda = 33551 + 422\,(p' - p_0) - 160p_0 + 254\,(q' - q_0) - 48q_0.$$

Table V gives a complete list of all the bands which have been measured, the observed and calculated wave-numbers and the values of p_0, q_0, p' and q' for each band. The intensities are on an arbitrary scale from 0 to 10 and were estimated from three different plates at 555, 166 and 67 mm. ; bands up to number 39 from the first, up to number 90 from the second and the remainder from the third.

Table V.

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
1	32869	—	—	—	—	—	4	—
2	33097	33101	2	1	0	4	3	—
3	33250	33249	0	1	0	0	0	A_1
		33247	1	3	1	3	—	$b_3{}^{iii}$
4	33304	33303	2	2	3	1	1	—
5	33329	33329	1	3	3	0	5	d_3
6	33347	33343	1	1	1	1	2	$b_1{}^{i}$
		33351	2	1	3	0	—	—
7	33489	33489	0	3	2	0	1	C_3

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
8	33531	—	—	—	—	—	0	—
ν_0	—	33551	0	0	0	0	—	A_0
9	33566	—	—	—	—	—	3	—
10	33594	33597	1	1	1	2	4	b_1^{ii}
		33591	2	3	5	0	—	—
		33595	2	3	2	5	—	—
11	33647	33645	1	0	1	1	1	b_0^{i}
		33643	2	2	2	4	—	—
12	33721	33717	1	2	2	2	2	c_2^{ii}
		33725	2	2	4	1	—	—
13	33751	33751	1	3	4	0	2	e_3
14	33762	33765	1	1	2	1	4	c_1^{i}
		33763	2	3	3	4	—	—
15	33773	33773	2	1	4	0	6	—
		33777	2	1	1	5	—	—
16	33783	—	—	—	—	—	—	—
17	33792	33791	0	2	2	0	2	C_2
18	33898	33899	1	0	1	2	4	b_0^{ii}
		33897	2	2	2	5	—	—
19	33911	33911	0	3	3	0	1	D_3
20	33925	33925	0	1	1	1	5	B_1^{i}
		33923	1	3	2	4	—	c_3^{iv}
—	—	33973	0	0	1	0	—	B_0
21	33988	33985	1	0	0	4	1	a_0^{iv}
22	34023	34019	1	1	2	2	6	c_1^{ii}
23	34030	34027	2	1	4	1	0	—
24	34037	—	—	—	—	—	3	—
25	34056	34059	0	0	0	2	1	A_0^{ii}
		34053	1	2	4	0	—	e_2
		34057	1	2	1	5	—	b_2^{v}
26	34069	34067	1	0	2	1	6	c_0^{i}
		34065	2	2	3	4	—	—
27	34073	34075	2	0	4	0	1	—
28	34139	34139	1	2	3	2	1	d_2^{ii}
29	34148	34147	2	2	5	1	5	—
30	34178	34179	0	1	1	2	6	B_1^{ii}
		34177	1	3	2	5	—	c_3^{v}
31	34182	34187	1	1	3	1	1	d_1^{i}
		34185	2	3	4	4	—	—
32	34194	34191	2	1	5	0	0	—
33	34206	—	—	—	—	—	2	—
34	34223	—	—	—	—	—	—	—
35	34227	34227	0	0	1	1	5	B_0^{i}
		34225	1	2	2	4	—	c_2^{iv}
36	34239	34239	1	0	0	5	1	a_0^{v}
		34235	1	0	3	0	—	d_0
37	34266	34265	0	1	0	4	1	A_1^{iv}
		34266	2	3	6	1	—	—
38	34292	—	—	—	—	—	1	—
39	34305	34307	1	2	4	1	1	e_2^{i}
40	34321	34321	1	0	2	2	5	c_0^{ii}
		34319	2	2	3	5	—	—
41	34327	34329	2	0	4	1	5	—
42	34353	34355	1	1	4	0	8	e_1
		34353	2	3	5	3	—	—

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
43	34374	—	—	—	—	—	5	—
44	34395	34395	0	0	2	0	2	C_0
		34393	1	2	3	3	—	d_2^{iii}
45	34425	34427	1	3	5	1	3	f_3^{i}
46	34444	34441	1	1	3	2	4	d_1^{ii}
		34449	2	1	5	1	—	—
47	34469	34467	0	2	3	1	7	$\mathrm{D}_2^{\mathrm{i}}$
48	34480	34481	0	0	1	2	9	$\mathrm{B}_0^{\mathrm{ii}}$
		34479	1	2	2	5	—	c_2^{v}
49 *a*	34490	34489	1	0	3	1	—	d_0^{i}
49 *b*	34498	34497	2	0	5	0	3	—
50	34506	34505	0	3	2	4	6	$\mathrm{C}_3^{\mathrm{iv}}$
51	34530	34527	1	1	2	4	1	c_1^{iv}
52	34560	34561	1	2	4	2	1	e_2^{ii}
53	34567	34567	0	0	0	4	6	$\mathrm{A}_0^{\mathrm{iv}}$
		34568	2	2	6	1	—	—
54	34576	34575	1	0	2	3	8	c_0^{iii}
55	34584	34587	0	3	4	1	2	$\mathrm{E}_3^{\mathrm{i}}$
		34583	2	0	4	2	—	—
56	34609	34609	1	1	4	1	8	e_1^{i}
		34607	2	3	5	4	—	—
57	34617	34616	2	1	6	0	4	—
58	34624	34621	2	1	3	5	5	—
59 *a*	34634	34635	0	2	4	0	4	E_2
59 *b*	34639	34639	0	2	1	5	—	$\mathrm{B}_2^{\mathrm{v}}$
60	34649	34649	0	0	2	1	3	$\mathrm{C}_0^{\mathrm{i}}$
		34647	1	2	3	4	—	d_2^{iv}
61	34657	34657	1	0	4	0	5	e_0
		34655	2	2	5	3	—	—
62	34716	—	—	—	—	—	3	—
63	34725	34721	0	2	3	2	6	$\mathrm{D}_2^{\mathrm{ii}}$
		34729	1	2	5	1	—	f_2^{i}
64	34740	34735	0	0	1	3	2	$\mathrm{B}_0^{\mathrm{iii}}$
		34741	2	2	4	5	—	—
65	34746	34743	1	0	3	2	5	d_0^{ii}
66	34756	34755	0	3	5	0	4	F_3
		34759	0	3	2	5	—	$\mathrm{C}_3^{\mathrm{v}}$
67	34768	34769	0	1	3	1	5	$\mathrm{D}_1^{\mathrm{i}}$
		34767	1	3	4	4	—	e_3^{iv}
68	34801	—	—	—	—	—	1	—
69	34813	34815	1	2	4	3	2	e_2^{iii}
70	34817	34817	0	0	3	0	5	D_0
		34815	1	2	4	3	—	—
71	34821	34821	0	0	0	5	2	$\mathrm{A}_0^{\mathrm{v}}$
		34822	2	2	6	2	—	—
72	34833	34829	1	0	2	4	2	c_0^{iv}
		34837	2	0	4	3	—	—
73	34845	34848	1	3	6	1	2	g_3^{i}
74	34854	34855	0	1	2	3	2	$\mathrm{C}_1^{\mathrm{iii}}$
75	34863	34863	1	1	4	2	2	e_1^{ii}
		34861	2	3	5	5	—	—
76	34872	34870	2	1	6	1	1	—
77	34891	34889	0	2	4	1	1	$\mathrm{E}_2^{\mathrm{i}}$
78	34902	34903	0	0	2	2	8	$\mathrm{C}_0^{\mathrm{ii}}$
		34901	1	2	3	5	—	d_2^{v}

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
79	34910	34911	1	0	4	1	10	e_0^{i}
		34909	2	2	5	4	—	—
80	34936	34937	0	1	4	0	7	E_1
		34935	1	3	5	3	—	f_3^{iii}
		34936	2	3	7	2	—	—
81	34962	—	—	—	—	—	1	—
82	34976	34975	0	2	3	3	2	$\mathrm{D}_2^{\mathrm{iii}}$
83	34988	34989	0	0	1	4	4	$\mathrm{B}_0^{\mathrm{iv}}$
		34984	2	2	7	1	—	—
84	34997	34997	1	0	3	3	6	d_0^{iii}
85	35029	35031	1	1	5	1	7	f_1^{i}
		35032	2	1	7	0	—	—
		35028	2	3	6	4	—	—
86	35042	35043	2	1	4	5	1	—
87	35058	35057	0	2	5	0	3	F_2
88	35061	35061	0	2	2	5	6	$\mathrm{C}_2^{\mathrm{v}}$
89	35067	35069	1	2	4	4	3	e_2^{iv}
90	35072	35071	0	0	3	1	5	$\mathrm{D}_0^{\mathrm{i}}$
91	35140	35143	0	2	4	2	1	$\mathrm{E}_2^{\mathrm{ii}}$
		35142	2	2	8	0	—	—
92	35149	35150	1	2	6	1	6	g_2^{i}
93	35157	35157	0	0	2	3	8	$\mathrm{C}_0^{\mathrm{iii}}$
94	35169	35165	1	0	4	2	2	e_0^{ii}
		35172	2	0	6	1	—	—
95	35191	35191	0	1	4	1	3	$\mathrm{E}_1^{\mathrm{i}}$
		35189	1	3	5	4	—	f_3^{iv}
		35195	2	1	5	0	—	—
		35190	2	3	7	3	—	—
96	35220	—	—	—	—	—	1	—
97	35231	35229	0	2	3	4	3	$\mathrm{D}_2^{\mathrm{iv}}$
98	35239	35239	0	0	4	0	8	E_0
		35237	1	2	5	3	—	f_2^{iii}
		35238	2	2	7	2	—	—
99	35259	35259	2	0	5	3	2	—
		35255	2	3	9	0	—	—
100	35274	—	—	—	—	—	1	—
101	35280	35277	0	1	3	3	1	$\mathrm{D}_1^{\mathrm{iii}}$
		35282	2	3	6	5	—	—
102	35298	—	—	—	—	—	3	—
103	35309	35311	0	2	5	1	3	$\mathrm{F}_2^{\mathrm{i}}$
		35312	1	2	7	0	—	h_2
104	35318	—	—	—	—	—	4	—
105	35323	35325	0	0	3	2	7	$\mathrm{D}_0^{\mathrm{ii}}$
		35323	1	2	4	5	—	e_2^{v}
106	35332	35333	1	0	5	1	6	f_0^{i}
		35334	2	0	7	0	—	—
		35330	2	2	6	4	—	—
107	35347	35349	0	3	4	4	2	$\mathrm{E}_3^{\mathrm{iv}}$
		35345	2	0	4	5	—	—
		35348	2	3	8	2	—	—
108	35359	35359	0	1	5	0	7	F_1
		35356	1	3	6	3	—	g_3^{iii}
109	35378	35378	2	1	6	3	1	—
110	35395	35397	0	2	4	3	3	$\mathrm{E}_2^{\mathrm{iii}}$
111	35402	35404	1	2	6	2	1	g_2^{ii}

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
112	35413	35411	0	0	2	4	1	C_0^{iv}
113	35427	35430	0	3	6	1	2	G_3^{i}
		35426	2	0	6	2	—	—
114	35445	35445	0	1	4	2	2	E_1^{ii}
		35443	1	3	5	5	—	f_3^{v}
		35444	2	1	8	0	—	—
		35444	2	3	7	4	—	—
115	35451	35452	1	1	6	1	2	g_1^{i}
116	35474	35478	0	2	6	0	3	G_2
117	35483	35483	0	2	3	5	8	D_2^{v}
118	35492	35493	0	0	4	1	10	E_0^{i}
		35491	1	2	5	4	—	f_2^{iv}
		35492	2	2	7	3	—	—
119	35502	35500	1	0	6	0	1	g_0
		35505	1	0	3	5	—	d_0^{v}
120	35560	35565	0	2	5	2	1	F_2^{ii}
		35557	2	2	9	0	—	—
121	35570	35566	1	2	7	1	7	h_2^{i}
122	35580	35579	0	0	3	3	9	D_0^{iii}
123	35586	35587	1	0	5	2	1	f_0^{ii}
		35588	2	0	7	1	—	—
		35584	2	2	6	5	—	—
124	35592	35592	0	3	7	0	2	H_3
125	35615	35613	0	1	5	1	1	F_1^{i}
		35614	1	1	7	0	—	h_1
126	35625	35625	1	1	4	5	1	e_1^{v}
127	35648	35650	2	2	8	2	3	—
128	35654	35651	0	2	4	4	6	E_2^{iv}
129	35661	35661	0	0	5	0	10	F_0
		35658	1	2	6	3	—	g_2^{iii}
130	35700	35699	0	1	4	3	1	E_1^{iii}
		35698	2	1	8	1	—	—
		35698	2	3	7	5	—	—
131	35706	35706	1	1	6	2	1	g_1^{ii}
132	35730	35732	0	2	6	1	1	G_2^{i}
133	35736	—	—	—	—	—	6	—
134	35741	35745	1	2	5	5	4	f_2^{v}
135*a*	35748	35747	0	0	4	2	8	E_0^{ii}
		35745	1	2	5	5	—	—
135*b*	35753	35754	1	0	6	1	—	g_0^{i}
136	35778	35780	0	1	6	0	8	G_1
137	35814	35819	0	2	5	3	1	F_2^{iii}
		35811	2	2	9	1	—	—
138	35824	35820	1	2	7	2	1	h_2^{ii}
139	35833	35833	0	0	3	4	7	D_0^{iv}
140	35841	35841	1	0	5	3	5	f_0^{iii}
		35842	2	0	7	2	—	—
141	35892	35894	0	2	7	0	2	H_2
142	35906	35905	0	2	4	5	7	E_2^{v}
		35904	2	2	8	3	—	—
143	35915	35915	0	0	5	1	9	F_0^{i}
		35916	1	0	7	0	—	h_0
144	35938	35938	0	3	6	3	—	G_3^{iii}
		35934	2	0	6	4	—	—
		35935	2	3	10	1	—	—

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
145	35962	35960	1	1	6	3	—	g_1^{iii}
146	35980	35978	1	2	8	1	—	j_2^{i}
		35983	2	2	10	0	—	—
147	35990	—	—	—	—	—	8	—
148	36001	36001	0	0	4	3	10	E_0^{iii}
		36004	0	3	8	0	—	J_3
		36000	2	0	8	1	—	—
		36000	2	2	7	5	—	—
149	36032	36034	0	1	6	1	—	G_1^{i}
150	36064	36065	2	2	9	2	—	—
151	36073	36073	0	2	5	4	8	F_2^{iv}
		36074	1	2	7	3	—	h_2^{iii}
152	36082	36082	0	0	6	0	10	G_0
153	36091	36095	1	0	5	4	—	f_0^{iv}
		36091	1	3	9	1	—	k_3^{i}
154	36147	36148	0	2	7	1	—	H_2^{i}
155	36159	36158	2	2	8	4	7	Diffuse
156	36162	36166	1	2	6	5	2	g_2^{v} diffuse
		36161	2	0	9	0	—	—
157*a*	36169	36169	0	0	5	2	9	F_0^{ii} diffuse
		36170	1	0	7	1	—	h_0^{i}
		36166	1	2	6	5	—	—
157*b*	36175	—	—	—	—	—	—	—
158	36195	36196	0	1	7	0	8	H_1 diffuse
159	36214	36214	1	1	6	4	2	g_1^{iv}
160	36233	36232	1	2	8	2	5	j_2^{ii}
		36237	2	2	10	1	—	—
161	36246	—	—	—	—	—	—	Diffuse
162	36252	36254	2	0	8	2	—	Diffuse
163	36257	36255	0	0	4	4	7	E_0^{iv} diffuse
		36258	0	3	8	1	—	J_3^{i}
164	36307	36306	0	2	8	0	2	J_2
165	36321	36319	2	2	9	3	8	—
166	36334	36336	0	0	6	1	10	G_0^{i}
167	36340	—	—	—	—	—	—	—
168	36391	36393	1	2	9	1	—	k_2^{i}
169	36402	36402	0	2	7	2	3	H_2^{ii}
170	36410	36412	2	2	8	5	5	—
171	36424	36423	0	0	5	3	6	F_0^{iii}
		36424	1	0	7	2	—	h_0^{ii}
172	36449	36450	0	1	7	1	2	H_1^{i}
		36446	0	3	6	5	—	G_3^{v}
173	36460	36460	2	1	8	4	1	—
174	36478	—	—	—	—	—	2	—
175	36487	36486	1	2	8	3	10	j_2^{iii}
176	36498	36498	0	0	7	0	10	H_0 diffuse
177	36515	36512	0	3	8	2	1	J_3^{ii}
178	36518	36516	1	0	6	4	1	g_0^{iv}
		36518	1	3	10	1	—	l_3^{ii}
179	36574	36573	2	2	9	4	4	—
180	36586	36582	1	0	8	1	8	j_0^{i} diffuse
		36587	2	0	10	0	—	—
181	36592	36590	0	0	6	2	—	G_0^{ii} diffuse
182	36609	36608	0	1	8	0	5	J_1 diffuse
		36609	0	3	7	4	—	H_3^{iv}

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
183	36623	36621	2	1	9	3	1	—
184	36631	36630	1	1	7	4	5	h_1^{iv}
185	36643	36647	1	2	9	2	8	k_2^{ii}
186	36666	36669	2	0	9	2	4	—
187	36679	36677	0	0	5	4	6	F_0^{iv}
		36678	1	0	7	3	—	h_0^{iii}
188	36727	—	—	—	—	—	2	From here on all the lines are diffuse
189	36743	36743	1	0	9	0	8	k_0
		36740	1	2	8	4	—	j_2^{iv}
		36745	2	2	10	3	—	—
190	36753	36752	0	0	7	1	10	H_0^{i}
191	36816	36814	0	2	8	2	—	J_2^{ii}
192	36822	36819	1	2	10	1	5	l_2^{i}
193*a*	36833	36836	1	0	8	2	—	j_0^{ii}
193*b*	36846	36844	0	0	6	3	5	G_0^{iii}
		36845	0	3	10	0	—	L_3
194	36857	36853	1	3	9	4	1	k_3^{iv}
195	36890	—	—	—	—	—	4	—
196	36901	36901	1	2	9	3	6	k_2^{iii}
197	36910	36910	0	0	8	0	8	J_0
		36910	0	2	7	4	—	H_2^{iv}
198	36914	—	—	—	—	—	1	—
199	36937	—	—	—	—	—	2	—
200	36940	—	—	—	—	—	1	—
201	36995	36997	1	0	9	1	1	k_0^{i}
		36994	1	2	8	5	—	j_2^{v}
		36999	2	2	10	4	—	—
202	37005	37006	0	0	7	2	6	H_0^{ii}
203	37016	37016	2	0	8	5	8	—
204	37046	37042	1	1	8	4	1	j_1^{iv}
		37047	2	1	10	3	—	—
205	37054	—	—	—	—	—	6	—
206	37069	37068	0	2	8	3	8	J_2^{iii}
207	37077	37073	1	2	10	2	1	l_2^{ii}
208	37092	37098	0	0	6	4	1	G_0^{iv}
		37090	1	0	8	3	—	j_0^{iii}
		37095	2	0	10	2	—	—
209	37113	37116	0	1	8	2	1	J_1^{ii}
210	37137	—	—	—	—	—	1	—
211	37149	37147	0	2	10	0	4	L_2
212	37155	37155	1	2	9	4	6	k_2^{iv}
213	37165	37164	0	0	8	1	8	J_0^{i}
		37165	0	2	7	5	—	H_2^{v}
214	37170	37169	1	0	10	0	1	l_0
215	37243	—	—	—	—	—	—	—
216	37260	37260	0	0	7	3	4	H_0^{iii}
217	37273	37277	0	1	9	1	6	K_1^{i}
		37274	0	3	8	5	—	J_3^{v}
218	37308	—	—	—	—	—	—	—
219	37316	—	—	—	—	—	—	—
220	37325	37325	0	0	9	0	—	K_0
		37322	0	2	8	4	—	J_2^{iv}

Table V—(continued).

No. of line.	Wave-number cm.$^{-1}$.		Series.				Intensity.	Remarks.
	Observed.	Calculated.	p_0.	q_0.	p'.	q'.		
		37327	1	2	10	3	—	l_2^{iii}
221	37353	37352	0	0	6	5	—	G_0^{v}
		37353	0	3	10	2	—	L_3^{ii}
		37349	2	0	10	3	—	—
222	37399	37401	0	2	10	1	—	L_2^{i}
223	37413	37418	0	0	8	2	—	J_0^{ii}
		37409	1	2	9	5	—	k_2^{v}
224	37423	37423	1	0	10	1	—	l_0^{i}
225	37489	—	—	—	—	—	—	—
226	37527	37531	0	1	9	2	—	K_1^{ii}
227	37555	37555	2	1	10	5	—	—
228	37565	—	—	—	—	—	—	—
229	37579	37579	0	0	9	1	—	K_0^{i}
		37576	0	2	8	5	—	J_2^{v}
230	37665	37672	0	0	8	3	—	J_0^{iii}
231	37724	—	—	—	—	—	—	—
232	37732	—	—	—	—	—	—	—
233	37751	37751	0	0	10	0	—	L_0
234	37810	—	—	—	—	—	—	—
235	37838	37833	0	0	9	2	—	K_0^{ii}
		37835	1	2	10	5	—	l_2^{v}
236	37907	37909	0	2	10	3	—	L_2^{iii}
237	37965	—	—	—	—	—	—	—
238	37987	—	—	—	—	—	—	—
239	38004	38005	0	0	10	1	—	L_0^{i}
240	38037	38039	0	1	9	4	—	K_1^{iv}
241	38080	—	—	—	—	—	—	—
242	38146	—	—	—	—	—	—	—
243	38185	38180	0	0	8	5	—	J_0^{v}
		38185	1	0	10	4	—	l_0^{iv}
244	38246	—	—	—	—	—	—	—
245	38267	—	—	—	—	—	—	—
246	38292	38293	0	1	9	5	—	K_1^{v}
247	38311	—	—	—	—	—	—	—
248	38344	38341	0	0	9	4	—	K_0^{iv}
249	38360	—	—	—	—	—	—	—
250	38383	—	—	—	—	—	—	—
251	38459	—	—	—	—	—	—	—
252	38476	—	—	—	—	—	—	—
253	38543	—	—	—	—	—	—	—
254	38580	—	—	—	—	—	—	—
255	38662	—	—	—	—	—	—	—
256	38730	—	—	—	—	—	—	—
257	38779	—	—	—	—	—	—	—
258	38817	—	—	—	—	—	—	—
259	38886	—	—	—	—	—	—	—
260	38918	—	—	—	—	—	—	—
261	38956	—	—	—	—	—	—	—
262	38994	—	—	—	—	—	—	—
263	39208	—	—	—	—	—	—	—

The agreement between the calculated and observed values is generally very good. As already stated, the value of the interval α' from $p' = 0$ to $p' = 6$ is constant at 422 cm.$^{-1}$, but at $p' = 7$ it begins to diminish. For the calculations of the groups H, J, K, L, the observed values of the origins are accepted and the other bands are calculated from these observed heads.

5. *Theoretical Discussion.*

There are two fundamental frequencies in the absorption of ultra-violet light by phosgene: $\alpha_0 = 582$ and $\beta_0 = 302$ cm.$^{-1}$. The Raman spectrum gives three frequencies: $a = 567$, $b = 444$, and $c = 290$ cm.$^{-1}$. It is probable that the ultra-violet frequency α_0 corresponds to the Raman frequency a and β_0 to c, the Raman frequency 444 being unrepresented in the ultra-violet spectrum.

The infra-red absorption of phosgene in carbon tetrachloride solution has been examined in this laboratory by Mlle. Honneger,* and by Marton.† Six bands were found :—

$$\lambda \quad = 1{\cdot}11 \quad 1{\cdot}45 \quad 1{\cdot}85 \quad 2{\cdot}40 \quad 2{\cdot}73 \quad 4{\cdot}9 \quad \mu$$

$$1/\lambda = 9010 \quad 6896 \quad 5405 \quad 4167 \quad 3660 \quad 2040 \text{ cm.}^{-1}.$$

Marton (*loc. cit.*) has also examined the infra-red absorption spectrum of phosgene vapour and found the band $\lambda = 2{\cdot}73\ \mu$. As already mentioned, infra-red measurements are not sufficiently precise to afford accurate information concerning the Raman and ultra-violet frequencies.

It is very difficult to decide to which atoms the different vibration frequencies are due.

For formaldehyde, Henri and Schou (*loc. cit.*) have found two pairs of vibration frequencies :—

$$\alpha_0 = 1572{\cdot}3 \qquad \alpha' = 1231{\cdot}3$$

$$\beta_0 = 441 \qquad \beta' = 398$$

For acetaldehyde, Schou (*loc. cit.*) has found that there is only a single pair of frequencies :—

$$\alpha_0 = 825 \qquad \alpha' = 517$$

Now for phosgene are found :—

$$\alpha_0 = 582 \qquad \alpha' = 422$$

$$\beta_0 = 302 \qquad \beta' = 254$$

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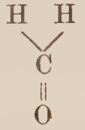
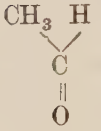
* "Untersuchung über die Absorption ultra-roten Strahlen," 'Dissert.,' Zürich, 1926.

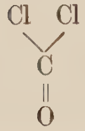
† 'Z. Phys. Chem.,' vol. 117, p. 97 (1925).

It is seen that the vibration frequencies decrease as the vibrating masses increase.

If the first period is due to the vibration of the groups other than the CO, then

for  $\mathrm{H_2C{=}O}$, the frequency H ←→ H = 1572·3 cm.$^{-1}$,

for  $\mathrm{CH_3(H)C{=}O}$, the frequency $\mathrm{CH_3}$ ←→ CH = 825 cm.$^{-1}$,

for  $\mathrm{Cl_2C{=}O}$, the frequency Cl ←→ Cl = 582 cm.$^{-1}$.

The frequency β_0 then corresponds to the vibration C ←→ O. This, however, is hypothesis and can be decided only by further experiments.

It has been found that in the activated molecule, the atomic vibration frequencies are less than those in the normal molecule signifying that the distance between the atoms increases.

It has been shown in the introduction that the *deformability* of a molecule can be measured by the relative variation of the quasi-elastic force between the vibrating atoms. This variation is equal to the value of

$$\frac{\alpha_0^2 - \alpha'^2}{\alpha_0^2} = 0{\cdot}47 \text{ for the vibration Cl} \longleftrightarrow \text{Cl}$$

and

$$\frac{\beta_0^2 - \beta'^2}{\beta_0^2} = 0{\cdot}28 \text{ for the vibration C} \longleftrightarrow \text{O.}$$

For the molecule of formaldehyde, Henri and Schou have found

$$\frac{\alpha_0^2 - \alpha'^2}{\alpha_0^2} = 0{\cdot}39, \qquad \frac{\beta_0^2 - \beta'^2}{\beta_0^2} = 0{\cdot}12.$$

And for acetaldehyde, this variation is

$$\frac{\alpha_0^2 - \alpha'^2}{\alpha_0^2} = 0{\cdot}61.$$

For the chlorine molecule Kuhn obtained

$$\frac{\alpha_0^2 - \alpha'^2}{\alpha_0^2} = 0{\cdot}90.$$

The molecule of phosgene is, therefore, more deformable than that of formaldehyde, but less than that of chlorine.

The same conclusion is reached from another consideration. The relative variations of the vibration frequencies are approximately equal to the relative variations of the moments of inertia. If the frequencies α_0, α' correspond to the vibration of the Cl-Cl atoms,

$$\frac{\alpha_0 - \alpha'}{\alpha_0} = \frac{J_0 - J'}{J_0} = \frac{582 - 422}{582} = 0 \cdot 28,$$

whereas for formaldehyde, the corresponding value is $0 \cdot 22$.

This great deformability of the phosgene molecule must be connected with the fact that the spectrum becomes diffuse after a small number of vibration states. It has been seen that the bands begin to become diffuse at group H ($p' = 7$) and that the diffusion increases very rapidly towards the ultra-violet.

At about $\lambda = 2700$, all the bands are already diffuse (Plate 5 (*b*)). The region of predissociation therefore begins between 2750 and 2700 A. This change in the character of the spectrum coincides with a diminution of the frequency α' which falls from 422 to 416 and then to 412 cm.$^{-1}$, signifying that, at this stage, the atoms of chlorine are mutually repelled.

It is known that the molecule of phosgene is decomposed by ultra-violet light of wave-length less than $\lambda = 2600$ A., the products being CO and Cl_2, as was first shown by Weigert.* The primary photochemical reaction is, however, not a simple separation of the chlorine molecule from carbon monoxide. We shall try to analyse the mechanism of the photochemical reaction.

The thermal decomposition of phosgene, which proceeds above 350°, has been studied by Christiansen,† and by Bodenstein and his school,‡ and it was found to proceed in stages :

$$COCl_2 \rightarrow COCl + Cl \rightarrow CO + Cl + Cl.$$

The energy of the complete reaction with formation of CO and Cl_2 has been determined by Thomsen ('Thermochem. Untersuchungen,' vol. 2, p. 359) who found the value 26,140 cals., and by Bodenstein and Plaut§ who found 26,200 cals.

The energy of dissociation of Cl_2 into atoms is 57,500 cals. Consequently the energy of decomposition of phosgene into normal CO and two atoms of chlorine is :

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* 'Ann. Physique,' vol. 24, p. 55 (1907).

† 'Z. Phys. Chem.,' vol. 103, p. 99 (1923).

‡ 'Z. Phys. Chem.,' vol. 110, p. 399 (1924), vol. 129, p. 241 (1927), vol. 130, p. 422 (1927), vol. 131, p. 153 (1927), and vol. B, 3, p. 459 (1929).

§ 'Z. Phys. Chem.,' vol. 110, p. 399 (1924).

$$COCl_2 \rightarrow CO + Cl + Cl - 84{,}000 \text{ cals.}$$

It has, however, been shown by Franck and confirmed by a large number of different observers that either one or both atoms produced by the photochemical dissociation of a molecule AB are in an electronically activated state. Heitler and Herzberg† have since shown that in similar cases, the dissociation of a normal molecule by increase of vibration without electronic activation produces one normal and one electronically activated atom, and that the dissociation of an activated molecule produces two normal atoms.

This occurs for example with CN, where we have

$$CN \text{ (normal)} \rightarrow C^* ({}^5S) + N ({}^4S)$$

and

$$CN \text{ (activated)} \rightarrow C ({}^3P) + N ({}^4S).$$

The direct dissociation of the normal carbon monoxide molecule gives two normal atoms

$$CO \text{ (normal)} \rightarrow C ({}^3P) + O ({}^3P)$$

The mechanism of the photochemical dissociation of phosgene is more complicated than that of diatomic molecules. The carbon atom in phosgene is tetravalent, and is therefore in the activated ^5S state. In carbon monoxide it is in the normal ^3P state. The CO group is, therefore, not in the same electronic state in phosgene (or in ketones and aldehydes) as in carbon monoxide. Consequently, the CO molecule combines with chlorine atoms to produce a molecule of phosgene only if it is activated, so that the electronic distribution in the carbon atom corresponds to a ^5S state.

The energy of the primary photochemical action must therefore be written :

$$COCl_2 + \text{light} \rightarrow CO^* + Cl + Cl - (84000 + x),$$

where x is the energy of activation of CO corresponding to the variation of carbon from its ^3P state to its ^5P state :

$$CO^* \rightarrow CO + x.$$

This active state of carbon monoxide is not the experimentally known active state of CO, which corresponds to 48478 cm.$^{-1}$ representing an energy of 140,000 calories, but another very unstable active state, which appears only as an intermediate state in the dissociation of ketones, aldehydes and phosgene.

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† 'Z. Physik,' vol. 53, p. 52 (1929), and vol. 57, p. 601 (1929).

The passage of C (^{3}P) to C (^{5}S) corresponds to an energy of about 1·6 volts = 37,000 calories. If the value of x were equal to 37,000 calories the energy of the reaction

$$COCl_2 \rightarrow CO^* + Cl + Cl$$

would be 84,000 + 37,000 = 121,000 calories. This corresponds to the wave-length $\lambda = 2380$ A., and the absorption in this region is continuous. We have seen, however, that the predissociation of the molecule of phosgene begins at about $\lambda = 2700$ A., which is equivalent to 106,000 calories. If this region corresponds to the limit of photochemical dissociation, then the active CO molecule formed corresponds to the energy :

$$x = 106{,}000 - 84{,}000 = 22{,}000 \text{ calories (1 volt).}$$

It is evident that this value is only a rough approximation, but it gives an order of magnitude which should not be very far from the correct value.

6. *Isotope Effect.*

It is known that the isotope effect appears in molecular spectra both in the rotation spectrum and the vibration spectrum.

The vibrational effect for diatomic molecules is given in a general formula established by Mulliken,[†] which may be written in the nomenclature already employed :

$$\Delta\nu = (1 - \rho)(p'\alpha' - p_0\alpha_0) - (1 - \rho^2)(x'\alpha'p'^2 - x_0\alpha_0 p_0{}^2),$$

where $\rho^2 = \mu_1/\mu_2$, μ_1 and μ_2 being the reduced masses of the two isotopes.

For polyatomic molecules the formula must be different, since the vibrations of the different atoms mutually influence each other, and it is certain that for such molecules the value of $\Delta\nu$ should be smaller than that calculated from the Mulliken equation.

In phosgene there are three types of molecules : $COCl^{35}Cl^{35}$ $COCl^{35}C^{37}$ and $COCl^{37}Cl^{37}$, in the ratio 11·3 : 6·7 : 1, since the two isotopes of chlorine exist in the ratio 3·35 : 1.

The bands corresponding to the three molecular isotopes should be distributed as triplets : on the side towards the red, a very feeble band corresponding to the isotopes 37-37, then a stronger one due to the isotopes 37-35, and on the side towards the ultra-violet a very strong band due to the isotopes 35-35.

These are clearly seen in the photomicrograms (figs. 1 and 3).

If the influence of the other atoms be neglected and the frequencies 582 and

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[†] 'Phys. Rev.,' vol. 25, p. 119 (1925).

422 cm.$^{-1}$ attributed to the chlorine atoms only, then (neglecting the band due to 37-37 which is very feeble)

$$1/\mu_2 = \tfrac{1}{35} + \tfrac{1}{35}, \qquad 1/\mu_2 = \tfrac{1}{35} + \tfrac{1}{37},$$

whence $1 - \rho = 0{\cdot}014$.

The values of $\Delta\nu$ calculated from Mulliken's equation for successive value of p' combined with $p_0 = 0$ are given in Table VI.

The separation of the doublets in the phosgene spectrum increases towards the ultra-violet as it should if they are due to isotopes. The observed separations are given in Table VI and it is seen that they are far less than those calculated from the Mulliken formula for a diatomic molecule.

Table VI.—Isotope separation for $p_0 = 0$.

p'.	$\Delta\nu$ calculated for diatomic molecules.	$\Delta\nu$ observed.
0	0	—
1	5·9	Small
2	11·8	3
3	17·7	5
4	23·6	6
5	29·5	8
6	35·4	9
7	—	9·5
8	—	10
9	—	10–12
10	—	13

Summary.

1. The Raman spectrum of phosgene is composed of three lines corresponding to the frequencies :—

$$a = 567 \quad b = 444 \quad c = 290 \text{ cm.}^{-1}.$$

2. The infra-red absorption spectrum of phosgene dissolved in carbon tetrachloride consists of six bands between 1·11 and 4·9 μ. Of these, the bands 1·11, 1·43, 1·77, 2·43 and 4·9 are also found in acetone and acetaldehyde. They are due to the carbonyl group CO. The band 3·1 to 3·2 μ which characterises the group CH is not found in phosgene, but is present in acetone and acetaldehyde.

3. The ultra-violet absorption spectrum of phosgene vapour consists of about 270 bands between 3050 and 2380 A. The absorption region is therefore the same as for all substances containing the carbonyl group. With aldehydes

and ketones, however, the absorption reaches a maximum at about 2800 A., whereas with phosgene it increases continuously towards the ultra-violet.

4. The bands are distributed at regular intervals in the spectrum. These are doublets or triplets with a separation of 0·5 to 1 Å. and also single bands.

5. The separation of the doublets increases towards the ultra-violet. The doublets can be attributed to the isotopes $COCl^{35}Cl^{37}$ and $COCl^{35}Cl^{35}$, the latter giving the more intense band on the ultra-violet side. The separation of the doublets is less than that for the chlorine molecules $Cl^{35}Cl^{37}$ and $Cl^{35}Cl^{35}$.

6. The absorption spectrum of phosgene is a vibration spectrum. The rotation lines are so closely spaced that they cannot be separated. The distribution of the vibration bands is represented very exactly by the formula:

$$1/\lambda = 33551 + 422p' - 582p_0 + 254q' - 302q_0$$

or

$$1/\lambda = 33655 + 422\,(p' + \tfrac{1}{2}) - 582\,(p_0 + \tfrac{1}{2}) + 254\,(q' + \tfrac{1}{2}) - 302\,(q_0 + \tfrac{1}{2}),$$

where $p_0 = 0, 1, 2$, and $q_0 = 0, 1, 2, 3$ are the vibrational quantum numbers of the normal molecule and $p' = 0, 1, 2 \ldots 12$ and $q' = 0, 1, 2, 3, 4, 5$, are those for the activated molecule.

7. The vibration frequencies of the normal molecule are $\alpha_0 = 582$ and $\beta_0 = 302$ cm.$^{-1}$ and those for the activated molecule $\alpha' = 422$ and $\beta' = 254$ cm.$^{-1}$. The values α_0 and β_0 correspond to the frequencies found in the Raman spectrum $a = 567$ and $c = 290$ cm.$^{-1}$.

8. The frequency $\alpha_0 = 582$ is similar to that found for the atoms in the molecule of chlorine, namely, $\alpha_0 = 565$ cm.$^{-1}$. Consequently, α_0 corresponds to the vibration of the chlorine atoms and β_0 to that of the CO group in phosgene.

9. The interval α_0 remains constant up to $p' = 6$, all the corresponding bands being sharp. At $p' = 7$ this interval diminishes and at the same time the bands become diffuse, the molecule being in a state of "predissociation." The distance between vibrating atoms is then increased.

10. The deformability of the molecule of phosgene is greater than that of formaldehyde but less than that of acetaldehyde and chlorine.

11. An activation of about 106,000 calories ($\lambda = 2700$) causes predissociation of phosgene, the bands becoming increasingly more diffuse and broader towards the ultra-violet. The photochemical decomposition of phosgene begins in this region.

12. The initial photochemical dissociation of phosgene is represented by the primary reaction:

$$COCl_2 \rightarrow CO^* + Cl + Cl,$$

with production of active carbon monoxide.

This active state corresponds to an energy of about 22,000 calories. It represents an electronic distribution analogous to that of a carbon atom in the ^5S state.

13. The electronic activation of similarly constituted compounds containing the CO group is :—

Formaldehyde ($H_2 . CO$)	$\nu_0 = 28280$ cm.$^{-1}$	$E_\epsilon = 80600$ cals.
Acetaldehyde ($CH_3H . CO$) ..	29409	83800
Propaldehyde ($C_2H_5H . CO$) ..	29350	83650
Phosgene ($Cl_2 . CO$)	33655	95900

We express our indebtedness to Mme. Henri for the enlargements of the photographs which have been made with great precision and also to Dr. Langseth for measuring the Raman spectrum.

The n-Fatty Acids.

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(Communicated by M. W. Travers, F.R.S.—Received January 14, 1930.)

The normal fatty acids may unquestionably be regarded as one of the most interesting and important groups of chemical compounds. Many of them occur commonly in nature, and form the basis of valuable industrial products. The part which they and their derivatives play in life processes gives them a particular interest to the biologist. As compounds, which appear to be readily obtainable pure, and which form regular series including a comparatively large number of individuals, they furnish the chemist and physicist with material peculiarly adapted for the study of the relationship between constitution and properties.

For these reasons they have been the subject of an almost endless number of investigations, in which the preparation and properties both of individual members or groups of individuals have been studied. At this stage, it might well have been assumed that every member of the series had long since been obtained pure, and its properties determined with so high a degree of accuracy, that only the exacting requirements of some new investigation would have demanded further study of the subject. Reference to the literature of the subject, however, showed that the real position was by no means satisfactory.

While, on the one hand, the results of the determination of such a property as the melting point of certain members of the series, for instance, arachidic acid, obtained from various natural sources by chemists of established reputation, gave a constant value, and while the criteria of purity of the various samples were quite satisfactory, the material was certainly not identical with samples of the corresponding acid prepared synthetically. The difference was in some cases such as to justify the assumption that the natural and synthetic acids were differently constituted, but no theory could be found to account for the observed differences.

Our attention was called to the matter in the course of an investigation on the oxidation of paraffin wax at low temperatures, when a number of acids was obtained, which appeared to be normal fatty acids, but which differed in their properties from synthetic acids, and which, at the same time, appeared to be perfectly pure. The usual laboratory methods, involving the fractional crystallisation or distillation of the acids and their salts and esters, were applied to the further purification of our products, but without result. We therefore decided to attack the problem in a new way. It appeared very probable that compounds which were unquestionably normal fatty acids could be obtained by certain well-established synthetic processes, and that if the products contained impurities, the nature of those impurities would at least be indicated by the nature of the processes used. We then proposed to determine the physical properties, and particularly the large crystal spacings, of these acids, and of certain of their derivatives, and also of mixtures of the various acids. Study of the naturally occurring products, and also of the products obtained by the oxidation of paraffin wax by the same process, would then, we hoped, lead to a solution of the problem before us.

The results of our investigation are described under the following headings :-

I. The synthetic fatty acids.
    (i) Methods of preparation.
    (ii) The melting and setting points of the pure acids, and of mixtures of known composition.
    (iii) The large crystal spacings of the pure acids, and of mixtures of known composition.
II. Fatty acids from the oxidation of paraffin wax.
III. Fatty acids from natural sources.
IV. Fatty acids from the oxidation of the alcohols present in Chinese wax and Carnauba wax.

PART I.—SYNTHETIC FATTY ACIDS.

(i) *Methods of Preparation.*

The *n*-synthetic acids were prepared in these laboratories, the acid containing 17 carbon atoms from pure palmitic acid, those containing 19, 20 and 21 from stearic acid, and those containing from 23 to 26 from behenic acid which was obtained by the reduction of erucic acid.

The palmitic and stearic acids (Kahlbaum's purest preparations) were converted into their ethyl esters, which were fractionated *in vacuo* until constant boiling fractions were obtained. The liquid ethyl ester of erucic acid, which can be readily purified, gave on reduction the solid ester of behenic acid. The esters were then reduced to their corresponding alcohols and these were converted into iodides. The iodides, through the nitriles, gave acids containing one additional carbon atom. By conversion of the iodides into the malonic acid derivative, and fusion of the resulting dicarboxylic acid, acids were obtained containing two carbon atoms more than the original alcohol employed in the synthesis.

Judging from the properties of the resulting acids and those of their potassium and acid potassium salts, and their ethyl esters, particularly the remarkable constancy of the large crystal spacings as determined by X-rays, they were of a high degree of purity.

(ii) A.—*The Melting and Setting Points of the Pure Acids.*

The melting points were determined on specimens previously melted into capillary tubes of outside diameter 1·45 ± 0·15 mm. The temperature was raised slowly until the material had partly melted, and was then allowed to fall until resolidification took place. The range of melting and solidification never covered more than 1°, and the same result could be repeated with an error of about ± 0·2°. In order to obtain the temperature of resolidification, some of the solid must be left in the tube. All temperatures were determined by means of a standard thermometer, and all have been corrected for emergent stem.

The melting points of the acids determined in this manner were close to the highest values recorded by Levene and others. But these values can be obtained with greater accuracy when larger quantities are available, and under these conditions, they are often alluded to as "setting points." We found a close correspondence between these data—determined by Garner, Madden and

Rushbrooke* (G in column 3, Table I), or by Garner and King in these laboratories† (K, column 3)—and either our melting points or the temperature at which resolidification took place.

In Table I, our values of the melting points of the acids are given in column 2, the setting points in column 3. The values of the melting points calculated from Garner's empirical formula (*loc. cit.*) are given in column 4, and the values obtained by Levene and Taylor‡ in column 5. Our values for the melting points of the ethyl esters are given in column 6, and those of Levene and Taylor in column 7.

Table I.—Synthetic *n*-Fatty Acids.

Carbon content of acid.	M.P.	Setting points.		Melting points.		
		Observed.	Calculated.	Acids (L. & T.)	Ethyl esters.	
					Observed.	L. & T.
C_{14}	54·0	53·7 G	56·4			
C_{15}	52·1	52·1 G	54·3			
C_{16}	63·1	62·3 G	64·4		25·0	
C_{17}	62·0	60·8 G	62·7		28·0	
C_{18}	70·1	—	70·8	70·5–71·5	34·0	33–34
C_{19}	69·4	69·5 G	68·8	69–70	37·5	37–8
C_{20}	75·2	74·2 G	75·6	76–77	41·0	41·5–42·5
C_{21}	75·2	—	73·5	75–76	45·0	45–46
C_{22}	80·0	79·2 K	79·6	81–82	48·0	48·5–49·5
C_{23}	79·6	78·7 K	77·4	80–81	51·0	52–53
C_{24}	84·0	83·1 K	82·8	85–86	54·4	55·5–56·5
C_{25}	83·2	82·9 K	80·6	84–85	56·5	58–59
C_{26}	88·2	87·4 K	85·4	88–89	59·6	

The melting points of the ethyl esters plotted against the carbon content of the respective acid lie on a smooth curve. The differences between the melting points of the esters and those of the acids plotted against the carbon content of the acid lie on two straight lines, one for the even and the other for the odd acids. The corresponding data from Levene and Taylor's melting points of acids and esters are also shown in fig. 1.

The melting points of our specimens of the acids between C_{11} and C_{26} lie on two smooth curves, one for the odd, and the other for the even acids, a well-known phenomenon. But the point corresponding to the C_{26} acid melting at 88·2° is at least 0·5° above the curve for the even acids. Levene and Taylor also found that the melting point of this acid is 88–89°.

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* 'J. Chem. Soc.,' p. 2491 (1926).

† 'J. Chem. Soc.,' p. 1849 (1929).

‡ 'J. Biol. Chem.,' vol. 59, p. 905 (1924).

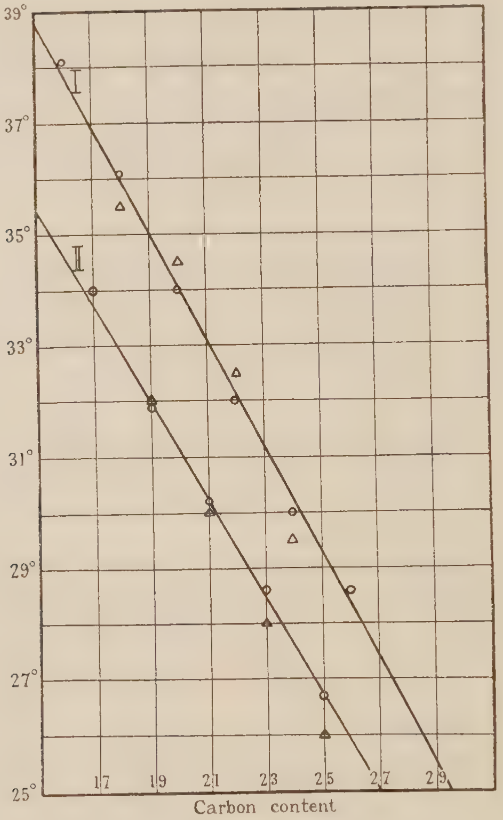

Fig. 1.—Δ M.P. Acid — M.P. Ethyl Ester.

I, Even Members. II, Odd Members. Δ, Levene and Taylor's Values.

It may be suggested that we have obtained this acid much purer than the other acids, but none of the facts supports this view.

We feel justified in stating that there is some evidence that the melting points of the acids, and particularly of those of high molecular weight, are not entirely independent of the treatment to which they are subjected during the process of melting and solidifying. In the case of the C_{24} acid, the value of the melting point obtained with finely powdered crystals is always higher than that obtained by the method described in this paper. This difference is not, however, observed in the case of the C_{26} acid.

In the case of acids containing odd numbers of carbon atoms, a very definite change appears to take place when the material is cooled to about 10° below the solidifying point, the material suddenly shrinking away from the glass of the tube or dish with which it is in contact. This phenomenon is only observed when using pure specimens of the acid. A parallel phenomenon is observed during the X-ray examination of the acid.

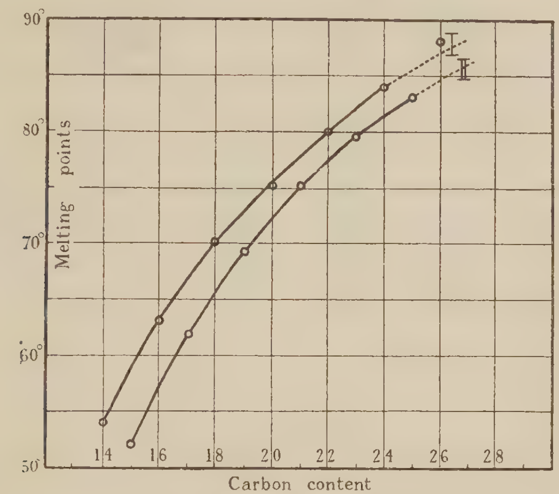

Fig. 2.—Melting Points of Acids.

I, Even Acids. II, Odd Acids.

(ii) B.—*The Melting Points of Mixtures of known Composition.*

With the exception of the melting points of various mixtures of palmitic and stearic acid, no data are available for the higher fatty acids, and since it was necessary for our purpose to have some information on this matter, a series of determinations was made on equimolar mixtures. We found that the melting points of all these mixtures were as sharp as those of the pure acids themselves, and, like these, the temperature at which resolidification took place lay within 1° of the melting points.

Table II gives the results of a series of determinations of the melting points of various equimolecular mixtures of acids (columns 1, 4 and 7) carried out under exactly the same conditions as those just described, and determined with the same degree of accuracy. Columns 3 and 6 show the difference between the melting points of the mixtures and that of the corresponding lower-acid constituent.

Table II.—Equimolecular Mixtures of *n*-Synthetic Acids.

Carbon content of acids.	M.P.	ΔM.P. of lower acid-mixture.	Carbon content of acids.	M.P.	ΔM.P. of lower acid-mixture.	Carbon content of acids.	M.P.
14+15	47·7	−6·3	14+16	48·3	−5·7		
15+16	54·6	+2·5	15+17	51·4	−0·7		
16+17	58·0	−5·1	16+18	57·0	−6·1	16+17+18	56·8
17+18	62·8	+0·8	17+19	59·2	−2·8	17+18+19	60·8
18+19	65·0	−5·1	18+20	64·6	−5·5	18+19+20	64·6
19+20	69·8	+0·4	19+21	67·0	−2·4	19+20+21	67·3
20+21	70·8	−4·4	20+22	70·8	−4·4	20+21+22	69·7
21+22	74·9	−0·3	21+23	72·7	−2·5	21+22+23	73·0
22+23	75·8	−4·2	22+24	75·7	−4·3	22+23+24	75·0
23+24	79·8	+0·2	23+25	77·1	−2·5	23+24+25	77·9
24+25	80·6	−3·4	24+26	79·8	−4·2	24+25+26	79·4
25+26	83·1	−0·1					

The melting points of the mixtures (column 2) where the acid with an even number of carbon atoms has the longer chain, when plotted against carbon content, lie on a smooth curve. Those in which the acid with an odd number has the longer chain, lie on a second curve which falls below the first (fig. 3).

Reference to Table I shows that the difference between the melting points

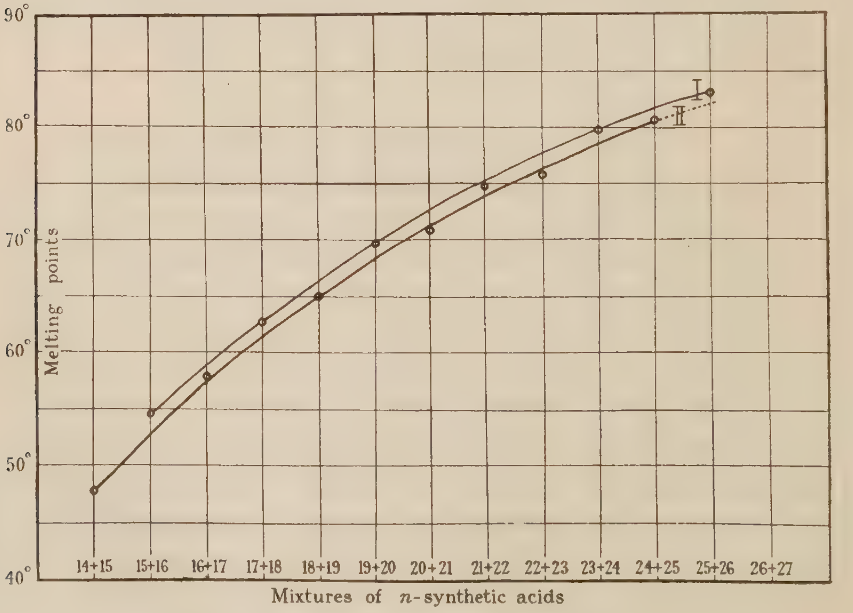

Fig. 3.—Melting Points of Mixtures of Acids.

I, Lower Member, Odd. II, Lower Member, Even.

of pairs of acids, of which the higher has an odd number of carbon atoms, is between 1·9° for the $C_{14} + C_{15}$ pair of acids, but falls gradually to 0·8° for the $C_{24} - C_{25}$ pair. It is therefore increasingly difficult to identify such acids by their melting points alone. But when (A) equimolecular amounts of these acids are mixed, the melting point falls from 6·3° C. below that of the lower acid in the case of a $C_{14} + C_{15}$ mixture, to 3·4° in the case of a $C_{24} + C_{25}$ mixture. On the other hand, when (B) equimolecular mixtures of acids with an odd number of carbon atoms and the next higher even acid are taken, the melting point is *raised* to 2·5° above that of the even acid in the case of the $C_{15} + C_{16}$ mixture, but only 0·2° in that of the $C_{23} + C_{24}$ mixture. Attention will be called, later, to a similar alternating effect associated with the spacings of the series.

The melting point of equimolecular mixtures of acids with an even number of carbon atoms is depressed below that of the lower member by 6·1° in the case of the $C_{16} + C_{18}$ mixture. The depression falls gradually to 4·2° in that of the $C_{24} + C_{26}$ mixture. On the other hand, in the case of mixtures of acids with odd numbers of carbon atoms, the melting point is only lowered 2·8° below that of the lower melting acid in the $C_{17} + C_{19}$ mixture, falling to 2·5° in the $C_{23} + C_{25}$ mixture.

The melting points of such pairs of acids as those just mentioned are altered but slightly by the addition to the mixture of the intermediate member, columns 5 and 8, Table II. For instance, an equimolecular mixture of $C_{21} + C_{23}$ acids fuses at 72·7°, and that of $C_{21} + C_{22} + C_{23}$ acids at 73·0°; the $C_{24} + C_{26}$ mixture melts at 79·8° and the $C_{24} + C_{25} + C_{26}$ mixture at 79·4°. These observations have a distinct bearing on the identification of an acid by comparing its melting point with that of artificial mixtures of known composition.

(iii) A.—*Large Crystal Spacings of Pure Acids.*

Series of long chain carbon compounds crystallise in forms which in any one series show a linear relationship between the spacings of the 001 planes and the number of carbon atoms in the chain.

In some series, the *n*-fatty acids, for instance, and, according to Müller, the *n*-paraffin hydrocarbons*, each member has two or more modifications with different spacings. Within certain limits, this linear relationship for each modification remains throughout the series, the particular form assumed by each acid depending mainly upon temperature.

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* 'J. Chem. Soc.,' vol. 127, p. 602 (1925).

The fatty acids actually constitute two series, one containing the even and the other the odd numbers of carbon atoms. The spacings that are important for the identification of the various acids discussed in this communication are those called B and C, see Table III.

Of these, B corresponds to the modification usually stable at room temperatures, and obtained when the acid crystallises from solutions, whereas C, in the case of acids with an *even* number of carbon atoms, corresponds to that form which separates from the molten material on cooling.

On the other hand, C, in the case of an odd numbered acid with 15 or more carbon atoms, is the spacing of a modification formed immediately after solidification. As the temperature falls, the transition point of such modifications is passed, and the B form appears.* This second form is only maintained in a metastable condition by very rapid cooling of the molten acid. Under such conditions, the substance contains both B and C forms, and judging from the intensities of the lines they are roughly in the proportions 2 or 3 to 1.

For the X-ray examination of an acid, a layer was obtained (*a*) by pressing crystals on to a glass slide, (*b*) by allowing a solution to evaporate, or (*c*) by melting the acid and allowing it to solidify. Photographs were then taken using the Kα line of iron or copper.

When the first or second method is used, the photograph shows the B spacing and sometimes, in the case of an acid with an even number of carbon atoms, the C spacing as well.

When the third method is used, the photograph shows the C spacing of an acid with an even number of carbon atoms, but both C and B may appear in the case of an acid with an odd number of carbon atoms.

With an acid containing an odd number, the C spacings can always be obtained if the temperature of the layer of acid is not allowed to fall more than a few degrees below its melting point, but if it falls further, the transition temperature is passed, and the photograph then shows the B spacing. It is possible that this transition temperature is indicated by the solid contracting away from the glass on cooling.

In experimenting with an unknown acid by the third method, it is therefore advisable to maintain a temperature not more than 2° below the melting point.

Under suitable conditions, a pure acid will show B and C spacings agreeing with those in Table III to within ± 0·5 per cent. The appearance of *both* spacings correct to within this limit, coupled with a correct melting point, are sufficient guarantee of a high degree of purity, but neither spacings or melting points considered separately are adequate.

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* de Boer, 'Nature,' vol. 119, p. 634 (1927).

Measurements of spacings have been published by several workers, but they vary considerably, the B spacing of margaric acid, for instance, lying between 36·9 and 41·4 Å.* J. Thibaud, who published measurements on the higher fatty acids,† does not give either their melting point or source, but, in our opinion, his values for the spacings of the acids of carbon content 17, 24, 27, 31 and 32 are too high for pure synthetic *n*-fatty acids. Possibly, in all these cases, he was dealing with mixtures. The values given in Table III were obtained by employing a uniform technique and using the synthetic acids prepared in this laboratory. The table also contains the spacings of the ethyl esters, potassium and acid potassium salts. The spacings of the acids and their esters are also shown in fig. 4.

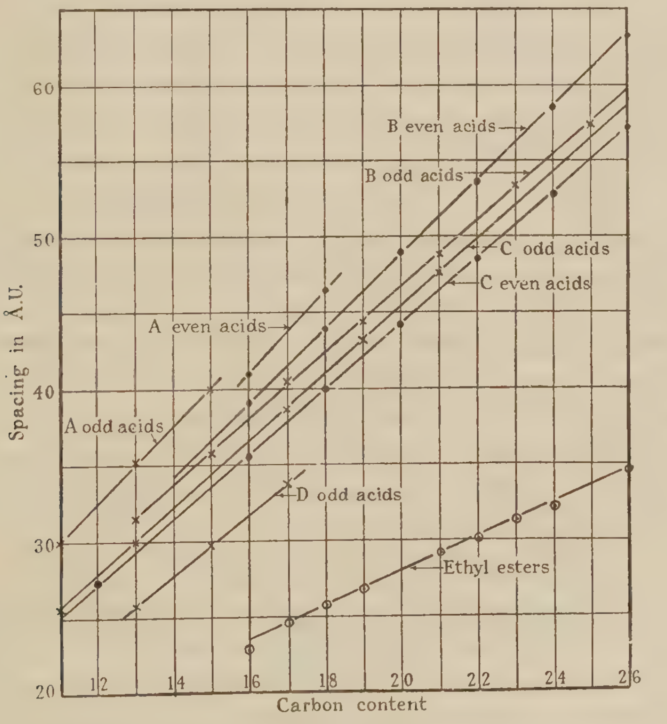

Fig. 4.—Number of Carbon Atoms in Acid Chain.

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* Müller, 'J. Chem. Soc.,' vol. 123, p. 2043 (1923); Müller and Shearer, *ibid.*, p. 3156; Shearer, *ibid.*, p. 3152; vol. 127, p. 599; Trillat, 'Theses,' Paris, 1926; Piper, Malkin and Austin, 'J. Chem. Soc.,' p. 2310 (1926); Piper, 'J. Chem. Soc.,' p. 234 (1929).

† 'Trans. Faraday Soc.,' vol. 25, p. 415 (1929).

Table III.—Spacings of Synthetic Fatty Acids and some Derivatives in Å., calculated from λKαFe = 1·9324.

Carbon content of acid.	X-ray spacings in Å.						
	Acid spacings.				Ethyl esters.	Potassium salts.	Acid potassium salts.
	B.	C.	A.	D.			
C_{12}		27·4				30·2	35·52
C_{13}	31·65	30·0	35·3	25·8		31·85	—
C_{14}	34·9*	31·5*				33·95	40·45
C_{15}	35·8	34·2	40·0	29·9		35·8	42·9
C_{16}	39·1	35·65	41·0		22·9	37·9	45·3
C_{17}	40·5	38·6		33·9	24·6	39·8	48·1
C_{18}	44·0	39·95	46·6		25·8	41·97	50·5
C_{19}	44·5	43·15			26·8	43·8	53·03
C_{20}	49·0	44·2			27·6*	46·45	55·65
C_{21}	49·0	47·8			29·2	47·85	58·35
C_{22}	53·6	48·5			30·1	50·7	60·8
C_{23}	53·4	51·8*			31·36	51·8	63·25
C_{24}	58·5	52·8			32·1	54·45	65·94
C_{25}	57·5	56·2*			33·5*		
C_{26}	63·3	57·3			34·6		
C_{27}	62·0	60·5			35·8		
C_{28}	68·2	61·4			37·0		
C_{29}	66·4	64·8			38·0		
C_{30}	73·0	65·8			39·2		

The data below the line in Table III, and those marked * were obtained by inter- or extrapolation.

Reference to Table III shows that in acids with a carbon content up to 23, the B spacings of an even acid and the next odd acid are nearly the same, but that there is a difference in the corresponding C spacings. The high spacings of 20 and 21, for example, are nearly 49·0 Å., but there is a difference of 3·6 Å. in their C spacings. After 24, however, the B spacings diverge considerably.

(iii) B.—*Spacings of Equimolar Mixtures of Acids.*

In crystals of the pure acids, the 001 planes are separated by the lengths of two molecules placed end to end with the carboxyl groups in contact. The spacings of equimolar mixtures of acids which are given in Table IV suggest that crystals can also be formed in which the two molecules have different carbon contents. We shall allude to these as mixed crystals.

The correspondence between the observed spacings in columns 2 and 4 with those interpolated from the respective pure acids in columns 3 and 5, Table 4, shows that mixed crystals are formed with remarkable ease in these

Table IV.—Spacings of Equimolecular Mixtures of Acids in Å.

Carbon content of mixture.	High spacing.		Low spacing.	
	Observed.	Interpolated for mixed crystals.	Observed	Interpolated for mixed crystals.
14+15	—	—	32·9	32·5
15+16	—	—	35·8	35·5
16+17	39·1	39·5	37·2	36·8
17+18	43·5	42·8	39·8	39·8
18+19	43·5	43·7	41·6	41·1
19+20	48·1	47·7	43·7	44·3
20+21	50·3	50·0	45·6	45·5
21+22	—	—	47·9	48·5
22+23	—	—	50·0	49·7
23+24	—	—	52·1	52·7

long chain acids. A fused equimolar mixture of acids with chains of n and $n + 1$ carbon atoms appears to crystallise with the molecule of n atoms joined carboxyl to carboxyl with that containing the $n + 1$ atoms. The spacing of such crystals falls on one of the C lines (spacings plotted against carbon content) exactly halfway between those of the acids containing the n and $n + 1$ carbon atoms. It is interesting that these mixed crystals tend to have alternately the habit of the odd and even acids, the form assumed being that of the *shorter* molecule. For instance, the combined molecules of the acids with 16 + 17 carbon atoms give a spacing which falls on the *even* C line at a point midway between the pure acids 16 and 17. But the mixture of acids with carbon contents of 17 + 18 gives a spacing on the *odd* C line also midway between those of the pure acids.

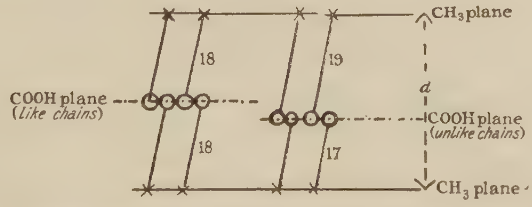

Fig. 5.—Suggested Packing (not to scale) of two 18 molecules and a 17 molecule with a 19 molecule to give the same spacing.

The chain axis may be perpendicular or inclined to these planes, and Shearer has shown* that this type of structure gives rise to an alternation in the intensities of the various orders of reflection, the odd orders being strong and the even orders weak.

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* 'Roy. Soc. Proc.,' A, vol. 108, p. 655 (1925).

The point of junction of a mixed pair of acids will not lie exactly halfway between the planes (see fig. 5) and, as we expected, it was found that the intensity distribution of such mixtures is not quite the same as those of the pure acids. High orders are rarely observed, although the reflections may be extremely sharp, showing that crystals of some size have been formed. If the mixed acids are allowed to crystallise from solution, they show sometimes a second modification corresponding to that of the B form of the pure acids. Here again, the combination spacing lies halfway between those of the pure acids, and appears to fall alternately on the B even and B odd line, but in such cases the crystals adopt the habit of the *longer* chain. Thus the B form of the acids of carbon contents 16 + 17 shows a spacing on the *odd* B line midway between those of the pure acids. On the other hand, in the case of the mixture 17 + 18, the B spacing lies on the *even* B line again midway between those of the pure acids.* This curious alternating effect, and that previously mentioned, may be compared with the corresponding effect noticed in the case of the melting points of the mixed acids. This alternation in the spacings is shown in fig. 6.

Chains of n and $n+2$ carbon atoms or n and $n+3$ also give rise to combination spacings, but equimolar mixtures of n and $n+4$ atoms as far as they have been examined—appear to crystallise separately.

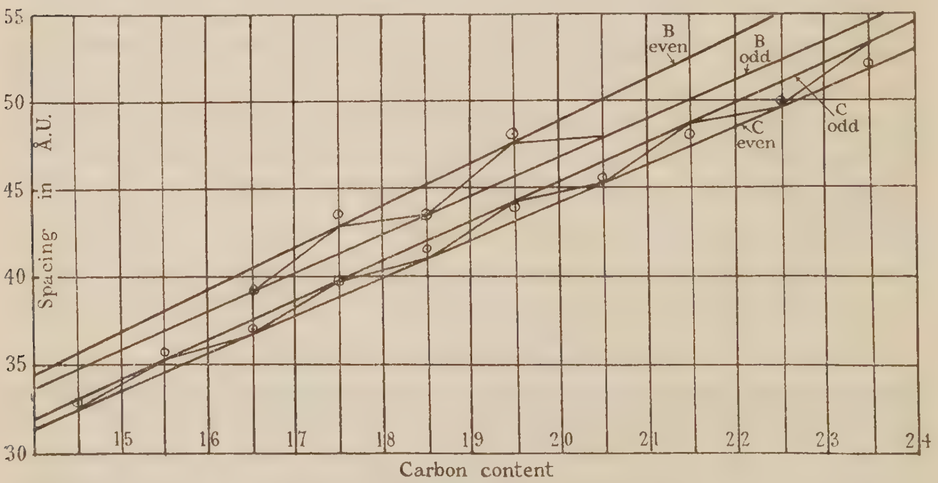

Fig. 6.—Spacings of Equimolar Mixtures.

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* 'Trans. Faraday Soc.,' vol. 25, p. 348 (1929).

The measurements of X-ray spacings of triple equimolecular mixtures of acids are given in Table V.

It is seen that equimolecular mixtures of n, $n + 1$, and $n + 2$ carbon atoms give crystals from the fused material showing a spacing nearly equal to that of the C form of the $n + 1$ chain. The whole mass of such crystals appears to be composed of those containing $n + 1$ carbon atoms and of mixed crystals of n and $n + 2$. This latter combination would be expected to have a length very nearly that of two $n + 1$ molecules.

Table V.—Spacings in Å. of Triple Equimolar Mixtures.

Carbon content of acids.	Spacing observed.	Carbon content of acid.	Spacing from Table III.
17+18+19	40·6	18	39·9
18+19+20	42·8	19	43·1
21+22+23	49·3	22	48·5
22+23+24	51·4	23	51·8
23+24+25	53·75	24	52·8

Some measurements have been made on the crystals obtained by mixing palmitic and stearic acids in different proportions.* The spacings of such mixtures lie between those of the pure acids and tend to the values of the component present in larger amount.

The ease with which mixed crystals are formed probably accounts for the difficulty, and, we believe in some cases, the impossibility of effecting the separation of mixed acids by fractional crystallisation.

Our measurements have shown that a mixture will not, as a rule, show as many orders of reflection as a pure acid, *and has in no case given the two spacings and the melting point* coinciding with those of a pure acid.

The curious phenomenon observed in the case of the mixed crystals of the ethyl esters of the fatty acids is illustrated in Table VI.

Table VI.—Spacings in Å. of Equimolecular Mixtures of Ethyl Esters.

Esters of acids with carbon content.	Spacing.	Pure ester with corresponding spacing.
18 + 19	29·2	$C_{21} = 29·1$
19 + 22	32·5	$C_{24} = 32·4$
21 + 23	34·0	$C_{25} = 33·5$
22 + 24	34·6	$C_{26} = 34·2$

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* ‘J. Chem. Soc.,’ 1926, p. 2310.

Equimolecular mixtures of ethyl esters show combination spacings corresponding to a chain containing *two carbon atoms more than that of the longer constituent*; for example, a mixture of, say, n and $n + 1$ carbon atoms has the same spacing as a pure ester with $n + 3$ atoms. This singular increase is, at present, under investigation, but there is some evidence that the spacing corresponds to a metastable phase.

The information gained from the study of the melting points and spacings of the acids and their mixtures has been used to interpret the corresponding data for the acids obtained from the oxidation of paraffin wax and from natural sources. The way in which this has been done will be considered in detail later, and it will suffice here to give a single example, that of specimen E (v), Table VIII, p. 236. In this case, the spacings 43·8 Å. and 39·9 Å. for a crystal layer, and 40·0 Å. for the solid after fusion, are all within 0·5 per cent. of those required for stearic acid, viz., B = 44·0 Å. and C 39·9 Å., but the melting point is 61° whereas that of stearic acid is 70·1°.

Now equimolecular combination spacings of $C_{17} + C_{18}$ are 43·5 Å. and 39·8 Å., and the melting point is 62·8°; consequently, the conclusion is drawn that this specimen is a mixture of these two acids rather than an impure preparation of stearic acid. In a similar manner, suggestions have been put forward for the composition of the other acids discussed in this communication.

Several of the interpretations of the nature of the mixtures have received striking confirmation from the spacings of their ethyl esters. Cerotic acid, for instance, was considered, from the spacings of the acid, to be a mixture of C_{26} and C_{28}. The spacings of the ethyl esters of this mixture were found to correspond to a chain of 30 atoms, exactly what would be expected from such a mixture.

The spacings of the potassium salts are a safe guide to the composition of the pure acids, but the crystals obtained from mixtures are so imperfect that it is difficult to obtain good photographs.

PART II.—FATTY ACIDS FROM THE OXIDATION OF PARAFFIN WAX.

Paraffin wax has been oxidised by a current of air at 100° C.,* and of the products containing oxygen, we found that between 58 and 70 per cent.—depending on the duration of the oxidation—consists of acids and oxy-acids.

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* 'J. Chem. Soc.,' vol. 121, pp. 496, 1520, 2804 (1922); vol. 125, p. 381 (1924); 1926, p. 2377.

Of this complicated mixture, between 17 and 20 per cent. are the monobasic acids, a description of which follows.

Previous observers, employing a higher temperature in the oxidation, have also isolated a large number of acids similar to many of those we have obtained.*

Further, some of these acids have been identified with arachidic, lignoceric and cerotic acids from natural sources.†

The majority of these acids, however, melt at temperatures distinctly lower than those recorded for the pure synthetic acids of similar carbon content. This divergence has led some of the above authors to consider that they were dealing not with normal, but with *iso-acids.*

We have no doubt, however, that all the acids we examined, obtained both from the oxidation of paraffin and from natural sources, are mixtures, and *mixtures of n-fatty acids.* We found no indication of the presence of iso-acids in any of our preparations.

It has been shown that the Scotch paraffin wax we employed is composed of a mixture of *n*-paraffins,‡ and these could not give rise to iso-acids on oxidation. Further, since the cerotic acid we isolated from the oxidation of this mixture of hydrocarbons, and also from synthetic *n*-triacontane, was identical with our preparation from beeswax, it would appear that the natural product also was composed of *n*-acids.

Finally, Shearer§ has shown that in the X-ray photographs side chains produce fluctuations in the intensity of the observed lines very different from those in the case of straight chains, and in no single case have such fluctuations been noticed during the examination of the many specimens of acids discussed in this communication.

Isolation and Analyses of Acids from the Oxidation of Paraffin Wax.

In a previous communication|| a method was described for the separation of the acidic from the neutral products of the oxidation of paraffin wax at 100°. It consisted in repeatedly extracting a strongly alkaline aqueous-alcoholic solution and suspension of the oxidation products with large quantities of light petroleum spirits.

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* Bergmann, 'Z. Angew. Chem.,' vol. 31, p. 69 (1918); Kelber, 'Ber. D. Chem. Ges.,' vol. 55, p. 1567 (1920); Fischer and Schneider, 'Ber. D. Chem. Ges.,' vol. 55, p. 922 (1920).

† Bergmann, *loc. cit.*; Kelber, *loc. cit.*; Franck, 'Chem. Z.,' vol. 49, p. 309 (1920); Francis and Wood, 'J. Chem. Soc.,' 1927, p. 1897.

‡ 'J. Chem. Soc., 1926, p. 1420; and 1927, p. 1897.

§ *Loc. cit.* and 'J. Chem. Soc.,' vol. 127, p. 591 (1925).

|| 'J. Chem. Soc.,' vol. 121, p. 560 (1922).

Source i.—The petroleum extracts the larger quantity of the inert materials, but there are always certain quantities of the alkaline salts of the acids suspended in it, and in the aqueous-alcoholic layer. When large amounts are being worked up these suspended salts form a valuable source of the acids of carbon content between 20 and 28. In the oxidation products from 12 kilos. of paraffin, they amounted to 260 grams, reduced to 150 grams after several crystallisations from chloroform.

Source ii.—The acids soluble in chloroform are purified by conversion into their methyl esters and distillation *in vacuo*. In one experiment, 43 grams of esters gave 31 grams boiling between 160° and 210° at 0·8 mm. pressure. The esters are purified by recrystallisation from ether and methyl alcohol. They are very soluble in the former and insoluble in the latter solvent. The acids obtained from them have a carbon content between about 16 and 22.

Source iii.—The crude acids obtained from the aqueous-alcoholic solution of their alkali salts are converted into lead salts, crystallised from alcohol, and those *insoluble* in the cold are recrystallised from benzene to remove inert material. The acids from these salts are converted into methyl esters, recrystallised from ether and methyl alcohol and then fractionated *in vacuo*. The acids present are composed of those of a carbon content between about 18 and 24. The total acids from *sources i* to *iii* form about 17 per cent. of the whole of the acidic products of the oxidation.

Source iv.—The acids whose lead salts are soluble in cold alcohol constitute about 80 per cent. of the acidic products of the oxidation; this amount increases with the duration of the process or if it is carried out at higher temperatures.

These acids form a thick, dark-coloured, liquid, and are converted into their methyl esters and distilled in a vacuum of 0·2 mm.; they give 43 per cent. of a distillate boiling up to 230° at 2 mm., which is composed of methyl esters of monobasic acids and inert material.

It was not possible to separate the constituents of this very complex mixture by fractionation *in vacuo*, but from certain fractions we isolated small quantities of acids of a carbon content between about 14 and 20.

Those acids mentioned above, whose esters either cannot be distilled without decomposition or boil at a much higher temperature than those mentioned, form a very complex group of mono- and poly-oxy acids. Although we repeatedly isolated substances from the crude acids by fractional precipitation of various salts, and these showed strikingly concordant properties, yet on preparing larger quantities we found that none of them was pure.

Isolation of Monobasic Acids from Sources i–iv.

The methods used for the isolation of various specimens of acids from the four sources mentioned, are briefly outlined below. The acids fall into six groups, A to F, and the spacings and other properties are given in two Tables, VII and VIII, which also contain the inferences we have drawn as to the carbon content of the acids comprising each specimen, for in no case was a pure acid obtained.

The crude mixture of acids from *source i*, purified by crystallisation from chloroform, fused at 73°, and formed a snow-white crystalline mass of acid value 154, and containing 77·9 per cent. C, 12·5 per cent. H ($C_{23}H_{46}O_2$ requires acid value 158, 78·0 per cent. C, 13·0 per cent. H). By a systematic and repeated recrystallisation from ether, this mixture was separated into four groups, the least soluble melting at 76° and giving an acid value 140, and the most soluble melting at 67°, with an acid value of 163. Although but a very partial separation was effected by this means, it proved of considerable value as a preliminary step in the isolation of the groups of acids detailed below.

The four fractions were separately converted into their methyl esters, but it was only from the first, by repeated recrystallisations from a mixture of ether and methyl alcohol, that it was found possible to isolate an ester, and from it an acid, with the ordinary characteristics of a pure material.

Acids—Group A.

(i) The most insoluble methyl ester melted at 62·5°, and on analysis gave C 79·6 per cent., H 13·3 per cent. ; $C_{29}H_{58}O_2$ requires C 79·4 per cent., H 13·2 per cent. The acid contained C 79·3 per cent., H 13·4 per cent. ; $C_{28}H_{56}O_2$ requires C 79·2 per cent., H 13·2 per cent.

(ii) Another specimen of this ester and acid was isolated from *source ii*. The methyl ester melted at 62°.

(iii) From the highest fraction of the esters from *source iii*, boiling point 220–230° at 1·5 mm., a methyl ester was isolated which, after purification, melted at 59°. It gave an acid which melted at 80°.

Specimen (iv) was obtained by the oxidation of synthetic *n*-triacontane.*

Acids—Group B.

(i) By the recrystallisation of the methyl esters from *source i*, a substance was finally obtained with a constant melting point of 58·5°. It gave an acid melting at 76°, containing C 79·1 per cent., H 13·3 per cent. $C_{26}H_{52}O_2$ requires C 78·8 per cent., H 13·1 per cent.

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* 'J. Chem. Soc.,' 1927, p. 1200.

(ii) A similar material was isolated from the more soluble acids of *source i*, by the fractionation of the methyl esters. These boiled at 190–200° at 0·1 mm. The acid melted at 77·5°. On analysis it gave C 77·8 per cent., H 12·9 per cent. $C_{24}H_{48}O_2$ requires C 78·3 per cent., H 13·0 per cent.

Acids—Group C.

(i) This specimen was obtained from the fractionation of the methyl esters from *source i*. These boiled between 222–226° at 3·3 mm., and the purified material melted at 53°. The acid on combustion gave C 78·0 per cent., H 13·1 per cent. $C_{23}H_{46}O_2$ requires C 78·0 per cent., H 13·0 per cent.

(Another specimen from *source ii*, melting point 74°, acid value 158, C 78·3 per cent., H 13·2 per cent. was not subjected to X-ray analysis.)

(ii) A similar acid was isolated from another fraction of the methyl esters boiling between 215–220° at 3·4 mm. from *source i*. The ester melted at 51–52°. The acid on combustion gave C 77·9 per cent., H 13·1 per cent.

The esters from *source i*, boiling between 212–215° at 3·2 mm., also gave an acid melting at 71°, of acid value 167. From *source ii*, on different occasions, two acids were isolated melting at 69 and 69·5° ; the former gave Å. 58·2, the latter Å. 58·3.

The melting points, column 3, acid values, column 4, and spacings of the acids, columns 6 and 7, in groups A, B, and C, are given in Table VII. Columns 8 and 9 contain the spacings of the potassium salts and ethyl esters of the specimens. Columns 5 and 10 contain comparisons, the former of the acid values, and the latter of the spacings of the ethyl esters of acids whose carbon content is stated. The last column contains our suggestions of the probable composition of the specimens.

It will be seen later that the acids in group A correspond closely to cerotic acid, melting point 77–80°, isolated from natural sources, and that specimen C_1 shows most of the characteristics of natural arachidic acid, melting point 74–75°.

An acid with an acid value of 152 and melting at 75° was obtained from the oxidation products of synthetic *n*-triacontane, and another with a value of 155 and melting at 74° from the same source. Probably both are mixtures similar to those in Table VII, C.

Table VII.—Acids from Oxidation of Paraffin Wax.

Group.	Specimen.	Melting point.		Acid value.		Spacings in Å.				Comparison.	Suggested composition of specimen of acid.
						Acid.					
		Observed.	Corresponding M.P.	Observed.	Corresponding to pure acid.	Pressed.	Melted.	K salt.	Ethyl ester.		
A	(i)	80·5		133	$C_{28}=132$	68·0			37·6	B of C_{28} $=68·2$ Ester of C_{29} $=37·8$	Chiefly 27 and 28.
	(ii)	77		146	$C_{26}=141$	68·4					28 and a lower acid.
	(iii)	80		133		68·8			39·0	Combined esters of C_{26} & C_{28} $=38·9$	Chiefly 26 and 28.
	(iv)	78		145		68·85	64·2		39·0		
B	(i)	76	C_{24+26} $=79·8$	153	$C_{25}=146$ $C_{24}=152$	63·8	53·5	59·8	35·7	B of C_{26} $=63·3$ C of C_{24} $=52·8$ K salt of C_{27} $=60·0$	22+24+26 & possibly 27.
	(ii)	77·5		159		63·8	54·35	57·9			
C	(i)	74	$C_{22+23+24}=75·0$	159	$C_{23}=158$	59·7	51·6	52·7		Melted spacing of $C_{22+23+24}$ $=51·6$	22+23+24 & some higher acid.
	(ii)	72·5	C_{22+24} $=75·7$	163	$C_{22}=165$	58·5	51·5	51·4	34·1	Ethyl esters of C_{22+24} $=34·6$ B of C_{24} $=58·5$	Chiefly 22+24.

Acids—Group D.

(i) The methyl esters from *source i*, boiling between 211 and 215° at 3·5 mm. gave an ester showing a constant melting point 47°.

(ii) From *source ii*, a similar ester was finally isolated from a fraction boiling from 158–166° at 0·1 mm. The pure ester melted at 47°, and gave an acid containing 77·0 per cent. C and 13·2 per cent. H. ($C_{21}H_{42}O_2$ requires 77·3 per cent. C and 12·9 per cent. H.)

From various more soluble residues of *source i*, and also from *source ii*, two similar acids were isolated; the methyl ester from the former melted at 46° and the acid at 71·5°, giving an acid value of 171. The latter gave an acid melting at 73° and containing 77·9 per cent. C and 12·5 per cent. H. An ester from *source iii*, obtained from a fraction boiling between 150–165° at 0·1 mm., after purification, melted at 48·5°, and gave 77·1 per cent. C and 13·1 per cent. H. The acid melted at 71·5° and gave an acid value of 179, C 77·0 per cent. and H 13·0 per cent. Although these acids were not subjected to X-ray analysis, there is no doubt that they belong to this group.

Acids—Group E.

(i) From the lower boiling fractions of the methyl esters from *source ii*, an ester was isolated and, after purification, gave an acid fusing at 62·4°.

(ii) From a fraction of the methyl esters of *source iii*, boiling between 180–200° at 2 mm., an acid was obtained melting at 66°.

(iii) An impure fraction of the methyl ester of *source ii*, boiling between 200–210° at 0·8 mm., gave esters from which the more soluble acid after purification melted at 64·5°, and on analysis gave C 76·4 per cent. and H 12·7 per cent.

(iv) *Source iii* yielded esters boiling between 150–160° at 0·1 mm. These were purified by recrystallisation and gave an acid melting at 67°, and giving C 76·8 per cent., H 12·8 per cent. ($C_{19}H_{38}O_2$ requires C 76·5 per cent., H 12·7 per cent.)

(v) A fraction from *source iv*, boiling between 202·5° and 205° at 14 mm., was freed from inert oxidation products present and finally gave an acid fusing at 61° with an acid value of 188.

Acids—Group F.

These acids were isolated from various fractions obtained in the fractionation of the methyl esters from *source iv*. The acids were freed from neutral material, and, as far as the amount allowed, purified by repeated recrystallisations until both melting point and acid value were constant.

(i) The impure methyl ester boiled at 190–192·5° at 14 mm., and from this, two acids were isolated ; the first melted at 60·5°,

(ii) and the second melted at 58·5° ; on analysis it gave C 76·1 per cent., and H 12·8 per cent. $C_{18}H_{36}O_2$ requires C 76·0 per cent. and H 12·7 per cent.

(iii) Two acids were also isolated from the esters boiling at 187·5–190° at 14 mm. The first melted at 60°,

(iv) and the second, melting at 57·5°, gave on analysis C 75·1 per cent., H 12·6 per cent. $C_{16}H_{32}O_2$ requires C 75·0 per cent., H 12·5 per cent.

The results are tabulated below in a manner previously described in Table VIII.

We have shown that it is possible to isolate from the very complex mixture of acids resulting from the oxidation of paraffin wax, a series of specimens which show some of the characteristics of pure acids.

For instance, the melting points of specimens A_{i} and A_{iii} only differ by 2° and their acid values are identical and agree with that for an acid $C_{28}H_{56}O_2$, which is 132. The *n*-fatty acid of this carbon content has not been synthesised, but it might be expected to melt in the neighbourhood of 90°.

Again, the acids E_{ii} and E_{iv} melt within 1° of each other and their acid values are 182 and 185. Fischer and Schneider isolated an acid closely resembling these, which melted at 65·5° and which they believed was $C_{19}H_{38}O_2$, whose acid value is 188. The synthetic *n*-fatty acid of this carbon content melts at 69·4°.

As a final illustration, the specimen F_{iii} may be taken, melting at 60°, with an acid value of 214. Kelber appears to have isolated the same acid melting at the same temperature, and which he considered was $C_{16}H_{32}O_2$, whose acid value is 219. The *n*-synthetic fatty acid of this content melts at 63·1°.

Tested by the old criteria, many of the acids described in Part II might well be regarded as pure individuals. But as their melting points were all lower than those of the corresponding *n*-fatty acids, they had either been insufficiently purified, or belonged to another series.

It was only when our specimens were subjected to an X-ray analysis, that the spacings of all the various specimens showed that we were dealing with mixtures of acids in every case. For reasons which have already been stated,

Table VIII.—Acids from Oxidation of Paraffin Wax.

Group.	Specimen.	Melting point.		Acid value.		Spacings in Å.				Comparison.	Suggested composition of specimen of acid.
		Observed.	Corresponding M.P.	Observed.	Corresponding to pure acid.	Acid.		K salt.	Ethyl ester.		
						Pressed.	Melted.				
D	(i)	72	C_{20+22} = 70·8	171	C_{21} = 172	54·2	48	49·1	31·5	B of C_{22} = 53·6 C of C_{22} = 48·5	20+22 and a longer chain, probably 24.
	(ii)	70		179		52·2	47·9			Ethyl ester of C_{23} = 31·3	20+22.
E	(i)	62·4	$C_{18+19+20}$ = 64·6	189	C_{19} = 188	44·8				B of C_{18} = 44·0	18+19+20.
	(ii)	66	C_{19+21} = 67·0	182	C_{20} = 179	47·4	42·7			Pressed C_{19+21} = 47·0	18+19+21.
	(iii)	64·5		182			44·76	47·36		Melted C_{19+21} = 45·2	
	(iv)	67	$C_{19+20+21}$ = 67·3	185		43·6	44·1				
	(v)	61	C_{17+18} = 62·8	188	C_{18} = 197	{43·8 39·9	40·0			C of 17+18 = 39·8 B of 17+18 = 43·5	17+18.
F	(i)	60·5	$C_{17+18+19}$ = 60·8	195	C_{18} = 197	40	40·1	39·8		$C_{17+18+19}$ = 40·6	17+18+19.
	(ii)	58·5		200		43·04	38·9	40·0			
	(iii)	60	C_{17+18} = 62·8	214	C_{17} = 207	43·5	39·4			B of C_{18} = 44·0 C of C_{18} = 40·0	Chiefly 17+18, but shorter chain present.
	(iv)	57·5	C_{16+17} = 58 C_{16+18} = 57	213	C_{16} = 219	35·9	35·8			C of C_{16} = 35·7	Chiefly 16+17, but 18 probably present.

the specimens were mixtures of *n*-fatty acids, and the divergence of their melting points from those of the pure acids, was due to this fact.

During the prolonged investigation of the acids described in Part II, the following have taken part in the work : Dr. H. H. T. Alway, Dr. C. H. Christie, Mr. V. L. S. Charley, Dr. E. Jefferis, Dr. R. W. Wallington, Mr. E. M. Wilkins.

PART III.—FATTY ACIDS FROM NATURAL SOURCES.

Arachidic, lignoceric and cerotic acids are a group of well-known substances repeatedly isolated from various natural sources over a long period of time. But again, the melting points of these acids are lower than those of the pure *n*-synthetic fatty acids to which each is supposed to correspond. For this reason, for instance, Stuewer in 1922 concluded that arachidic acid was *iso*-docosanic acid, $C_{22}H_{44}O_2$, and thought that it was closely related to lignoceric acid, which was *iso*-tetracosanic acid, $C_{24}H_{48}O_2$*. Levene, Taylor and Haller† prepared lignoceric acid fusing at 81° from peanut oil and also from cerasin, and stated that this acid was *isomeric* with synthetic *n*-tetracosanic acid. We do not believe, however, that it is possible to isolate a pure acid of a carbon content of 24 from the former source.

Several formulæ have been assigned at different times to cerotic acid, fusing between 77° and 80°. Marie in 1895 thought it was $C_{25}H_{50}O_2$, but at the present time it is believed to be $C_{26}H_{52}O_2$. Here again, if this latter formula is correct, it fuses about 8° below the synthetic *n*-acid of this carbon content.

At various times, different investigators have isolated small quantities of higher or lower acids from the group just discussed, but these have been regarded as impurities and no suggestion has yet been made that the acids termed arachidic, lignoceric and cerotic are themselves mixtures of acids of different carbon content.

In all cases, the carbon content of the acids under discussion has been determined by relying—in the early period of their isolation—on their ultimate analyses, and those of their salts and derivatives, and later, in addition, on the estimation of their molecular weights determined by titration with an alkali (often expressed as their acid values). It is clear, however, that both ultimate analyses and acid values can give but little information as to the nature of certain mixtures.

The confusion that exists as to the carbon content and nature of such acids, determined by the above methods, is well shown in the case of arachidic acid.

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* ' J. Prak. Chem.,' vol. 105, p. 199 (1922).

† ' J. Biol. Chem.,' vol. 61, p. 157 (1924).

which for 70 years was supposed to have a content of 20, apparently confirmed by its synthesis in 1884 by Schweizer. But Ehrenstein and Stuewer showed in 1923 that it corresponded much more closely to an acid of carbon content 22, although it was not identical with the *n*-acid. Again, Cohen in 1925[*] went back to a content of 20, whereas Holde, Bleyberg and Rabinowicz in 1929[†] stated that it was *n*-docosanic acid, $C_{22}H_{44}O_2$.

That such acids as those now discussed are mixtures has appeared doubtful owing to the fact that they have been repeatedly isolated, and both acid and derivatives shown to have the same melting points. Our specimen of cerotic acid from beeswax, its methyl and ethyl esters, amide and anilide, all fused at temperatures recorded in the literature, and, consequently, it appeared certain that our preparation was identical with those previously isolated by other observers. However, when our preparation was examined by X-rays, it was found to be a mixture of acids with a carbon content of 26 and 28.

Our observations on the melting points of equimolar mixtures of acids show that too much reliance cannot be placed on them for purposes of identification. For instance, acids of carbon content 20 and 21, and the following mixtures, 21 + 22, 22 + 23, 22 + 23 + 24, all melt between the limits of 74·9 and 75·2°.

1. *Arachidic Acid.*

Arachidic acid from oil of arachis (earth-nut oil) has been repeatedly examined since its first detailed description by Gossman in 1854.[‡] Believed to consist of the *n*-fatty acid $C_{20}H_{40}O_2$, and fusing between the limits of 74° and 77°, the original observations appear to have been confirmed—among others—by Caldwell,[§] Tassinari,[||] and compared for the first time in 1884 with the synthetic acid of the same carbon content by Schweizer.[¶] More recently, it has again been regarded as identical with the *n*-fatty acid $C_{20}H_{40}O_2$ by W. D. Cohen (1925).

On the other hand Kreiling in 1888[**] and Holde and Godbole in 1926[††] showed the presence in arachidic acid of acids with a carbon content of 24, melting at 80·5° to 81° and 26, melting at 78·5–79°. In 1923, Ehrenstein

[*] 'Proc. K. Akad. Amsterdam,' p. 63 (1925).

[†] 'Ber. D. Chem. Ges.,' vol. 62, p. 177 (1929).

[‡] 'Liebig's Annalen,' vol. 89, p. 1 (1854).

[§] 'Liebig's Annalen,' vol. 101, p. 97 (1857).

[||] 'Gazz. Ital. Chim.,' vol. 8, p. 305 (1878).

[¶] 'Arch. Pharm.,' vol. 22, pp. 222, 1767 (1884).

[**] 'Ber. D. Chem. Ges.,' vol. 21, p. 880 (1888).

[††] 'Ber. D. Chem. Ges.,' vol. 59, p. 36 (1926).

and Stuewer* isolated arachidic acid from earth-nut oil obtained from two sources, found that both specimens fused at 75°, and concluded that it was $C_{22}H_{44}O_2$, but was *iso*-docosanic and not the normal acid. But more recently, Holde, Bleyberg and Rabinowicz† have again investigated this problem and state that the acid is *normal* docosanic.

This brief outline of the literature on arachidic acid shows the conflicting opinions which have been expressed as to its nature, and indicates clearly the unreliability of the old methods employed to establish the carbon content of the higher acids obtained from natural sources.

That arachidic acid is not identical with the synthetic *n*-fatty acid $C_{20}H_{40}O_2$ is certain, and that it contains small quantities of different acids appears to be established. At various times, those with carbon contents of 21, 24, 25 and 26 have been described. Our investigations, however, show that arachidic acid itself is a mixture, and they give some indications of the nature of the acids comprising the mixture.

We leave open the question of the nature of the acid termed "arachidic" isolated from sources other than oil of arachis. Baczewski,‡ for instance, obtained an acid from *Nephelium Lappaceum* (Java) fusing at 77° (n-$C_{20}H_{40}O_2$ melts at 75·2°) and described a large number of derivatives, and the analyses of these agree so remarkably well with an acid of carbon content 20 that it is possible that the author was actually dealing with an acid $C_{20}H_{40}O_2$, or with a mixture in which this acid largely predominated. But the uncertainty previously alluded to will remain until the X-ray spacings of the acid from such a source have been determined.

Specimen I.—The first preparation was made in these laboratories by Mr. L. T. Darch from 2·4 kilos. of oil of arachis. The crude solid acids were converted into their ethyl esters and fractionated. The higher fractions gave a yield of about 4 per cent. of the so-called arachidic acid melting at 73·5°. The esters of the acid melting at this temperature were repeatedly fractionated and finally gave two specimens (A) boiling point 212–212·5° at 3·5 mm., melting at 52° and giving an acid fusing at 75°. The acid value was 161, C = 77·2 per cent., H 13·2 per cent. ($C_{22}H_{44}O_2$ has acid value 165, C 77·6 per cent., H 12·9 per cent.) The second specimen (B) boiled between 225 and 230° at 4·5 mm., melted at 54° and gave an acid melting at 78·5°, acid value 151, C = 77·9 per cent., H 12·9 per cent. ($C_{24}H_{48}O_2$ has acid value 152,

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* 'J. Prak. Chem.,' vol. 105, p. 199 (1922).

† 'Ber. D. Chem. Ges.,' vol. 62, p. 177 (1929).

‡ 'Monat.,' vol. 17, p. 528 (1896).

C 78·3 per cent., H 13·0 per cent.) This higher acid was converted into its acid potassium salt; this was repeatedly extracted with boiling benzene and the acid finally obtained (specimen B_1) again examined by X-rays. Its melting point was unaltered by this treatment.

Specimen II.—The second preparation of arachidic acid has been obtained from Messrs. Schuchardt; its origin was oil of arachis.

After several crystallisations, it melted at 73° and its recrystallised ethyl ester at 52·5°. The acid gave an acid value of 155 and contained C 78·2 per cent., H 12·9 per cent., and its ethyl ester 78·4 per cent. C and 12·9 per cent. H. These data are close to those required for the acid $C_{23}H_{46}O_2$, acid value 158, C 78·0 per cent., H 13·0 per cent.; ethyl ester C 78·5 per cent., H 13·1 per cent.

The small residues obtained from the recrystallisation of the ethyl esters melted at 45·3°, and as this remained constant on repeated crystallisations, the specimen (C) was submitted to X-ray analysis. The acid from this melted at 73°.

A preliminary fractionation of 42 grams of the esters gave fractions boiling between 219° and 229° at 3·5 mm., and melting between 43·5° and 52·5°. There were 12 grams boiling between 219° and 224°, 22 grams between 226° and 228° and a residue of 6 grams which on purification melted at 57° and gave an acid melting at 78·5°—Specimen I.

A systematic fractionation was then carried out with the relatively small amounts of esters at our disposal, and finally we obtained fractions, and from them the corresponding acids, which were repeatedly recrystallised before they were examined by X-rays. The residue left after the fractionation melted, after purification, at 54·5°; its boiling point was above 232° at 2 mm., and the acid melted at 78·5°—Specimen H. The fractions were as follows:—

Specimen D.—Boiling point 219–220° at 3 mm., giving an acid melting point 74°.

Specimen E.—Boiling point 220–224° at 3 mm., giving an acid melting point, 75°.

Specimen F.—Boiling point 224–226° at 3 mm., giving an acid melting point 77°.

Specimen G.—Boiling point 230–232° at 2·5 mm., giving an acid melting point 78°.

In the following Table IX we give the results of an X-ray examination of these various fractions, of some of the recrystallised acids obtained from them,

Table IX.—Arachidic Acid.

Specimen.	M.P.	Comparison M.P.	Spacings in Å.				Suggested composition of specimen of acid.
			Acid.	Comparison acid.	Ester.	Comparison ester.	
I—A	75	C_{22+24} =75·7 $C_{22+23+24}$ =75·0	51·6	C of C_{22+24}=50·7	31·8 34·4	C_{24} =32·1 C_{26} =34·6	22+24. Latter in excess.
B	78·5	C_{24+25} =80·6 C_{24+26} =79·8	57·85	B of C_{24}=58·5 B of C_{25}=57·5			Probably 24+25.
B_1	78·5	C_{24+25} =80·6	57·2				24+25.
II—C	73	C_{21+23} =72·7	51·7	C_{21+23} =51·8	33·1	C_{21+23}=34·0	21+23.
D	74	C_{22+24} =75·7	51·6		31·8 29·7		22+24. First predominating.
E	75				32·7		Probably 22+24.
F	77	C_{23+25} =77·1	56·3	C_{23+25} =54 C_{25} =56·2	35·04		Chiefly 23+25 with acid of longer chain.
G	78				35·55		Same as F, but larger quantity of higher acid.
H	78·5	C_{24+26} =79·6			36·2	C_{24+26}=36·5	24+26.
I	78·5		59·0	B of C_{24} =58·5			24+26; first predominating.

and the suggested composition of each specimen. It is clear that with the amount of acid originally available, viz., 45 grams, no separation of pure individual esters had been attained, if indeed, separation by this method alone is possible. Holde, after describing the results of the fractionation of the ethyl esters of montanic acid* concluded that separation was not possible.

Morgan and Holmes† have obtained spacings for various specimens of arachidic acid which varied from 50·4 Å. to 58·4 Å., and for an acid fusing at 77°, 54·5 Å. Thibaud (*loc. cit.*) gives a spacing of 59·0 Å. for an arachidic acid whose origin and melting point were not stated.

II. *Lignoceric Acid.*

Meyer, Bird and Soyka in 1913‡ showed that lignoceric acid melting at 81° was not identical with the synthetic acid $C_{24}H_{48}O_2$ melting at 84·5°. Brigl and Fuchs in 1922§ isolated two acids from lignoceric acid melting at 80–81°, prepared from beechwood tar. One fused at 84·5° and the isomer about 11° lower.

We have not had the opportunity of isolating this acid ourselves, but Dr. Brigl sent us two specimens, labelled "lignoceric" and "iso-lignoceric" acids, together with a preparation of the synthetic acid, $C_{24}H_{48}O_2$.

The X-ray measurements of the synthetic preparation were identical with ours, 58·5 Å. and 52·8 Å., and both melted at the same temperature, 83·5°.

The acid from beechwood tar also melted at 83·4°, and its spacings were 58·4 Å. and 52·7 Å. The ethyl ester gave 32·9 Å., compared with the observed value of 32·1 Å. It is quite clear that the normal acid $C_{24}H_{48}O_2$ can be isolated in a pure condition from the source mentioned.

The iso-lignoceric acid melting at 74·5° gave the two spacings, pressed 57·2 Å. and melted 52·52 Å. It is certainly not a pure acid, and we suggest that it is a mixture of the *n*-acids, 23 and 24. The spacings of an equimolar mixture of these acids are 57·5 Å. and 52·0 Å., but the melting point is 79·8°. Probably these two acids are the main components of "iso-lignoceric acid," but some other acid is also present.

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* 'Umschau,' 1929, p. 105.

† 'Soc. Chem. Ind.,' vol. 47, p. 309 (1928).

‡ 'Monat.,' vol. 34, p. 1113 (1913).

§ Hoppe-Zeylen, 'Z. Phys. Chem.,' vol. 119, p. 280.

III. *Cerotic Acid.*

Brodie in 1848* considered that cerotic acid had a carbon content of 27; Schalfejew† confirmed this view, but found the presence of another acid with a content of 34 melting at 91°. Nafzger in 1884‡ concluded that the acid was chiefly composed of one with a content of either 26 or 27, and that the higher acid present was 30 or 31. Marie in 1896§ undertook a most careful and detailed investigation of "cerotic acid" from beeswax and showed that the ordinary material was mixed with melissic acid; the former melted at 77·9° and was $C_{25}H_{50}O_2$, and the latter $C_{30}H_{60}O_2$ melted at 90°.

In 1897, Henriques‖ stated that cerotic acid, melting at 78·5°, was unquestionably $C_{26}H_{52}O_2$. Kiesel in 1925¶ judged that the old values for the melting points of cerotic acid—between 77·5° and 81°—were too low, and succeeded in raising the value of the acid from beeswax to 83–84°, and isolated specimens of what he considered to be the same acid from the spores of two ferns. These melted at 85–85·5°, the highest recorded point for the acid.

This very brief sketch of the literature again shows a divergence of opinion as to the real nature of the acid. All the recorded data are incapable of leading to any decision between a carbon content for this acid of 25 or 26; and preference for the latter is largely based on the current belief that acids with an odd number of carbon atoms are not usually found in nature. That the acid is not identical with the synthetic normal acid $C_{26}H_{52}O_2$ is clear. The presence of higher acids is certain, but our knowledge of the carbon content of these is vague. No direct comparison between synthetic acids of a higher carbon content than 26 can be made, since none has yet been synthesised. It is in such cases that the straight line relationship existing between the spacings and the carbon content of the acids and their derivatives, enables a clue to be obtained.

We give below the data for specimens of so-called cerotic acid isolated from beeswax, oxidation of paraffin wax and *n*-triacontane, carnauba wax and Chinese wax.

Source i. Beeswax.—The first specimen of cerotic acid was prepared for us by the Eastman Kodak Company. It had been obtained from beeswax, the acids converted into their methyl esters and fractionated. The fraction boiling between 245° and 255° at 3 mm., melted at 58°, and gave an acid which after crystallising twice from carbon tetrachloride melted at 77·5°. This preparation melted at the same temperature as that given by Marie, although that of the methyl ester was 2° low.

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* 'Liebig's Annalen,' vol. 67, p. 180.

† 'Bull. Soc. Chem. Paris,' vol. 26, p. 450 (1876), and vol. 27, p. 372 (1877).

‡ 'Liebig's Annalen,' vol. 224, p. 225 (1884).

§ 'Ann. Chim. Phys.,' vol. 7, p. 145 (1896).

‖ 'Ber. D. Chem. Ges.,' vol. 30, p. 1415 (1897).

¶ 'Ber. D. Chem. Ges.,' vol. 58, p. 1386 (1925).

As this specimen might be contaminated with non-acidic substances, it was converted into its barium salt, which was successively extracted with acetone, benzene and finally ether. The acid recovered from its salt melted at 78° (Specimen A), and on analysis gave 78·6 per cent. C and 13·1 per cent. H, and its acid value was 144. ($C_{26}H_{52}O_2$ requires 78·8 per cent., 13·1 per cent. H, and acid value 141.)

The methyl ester was prepared by the usual method and also by the action of diazomethane. The former melted at 60°, the latter at 60·5°. The ethyl ester melted at 58°. Marie gave 62·0° for the former and 60·5° for the latter.

Finally, this preparation was steam distilled for a long period. Only traces of a solid passed over, and the resulting acid after crystallisation from benzene melted at 78·5° (Specimen B). An attempt to purify this specimen further by recrystallisation of its acid potassium salt gave an acid of the same melting point, but showing a rather higher spacing (Specimen B_1).

The purified preparation of cerotic acid, melting at 78°, was converted into its acid chloride and then into the amide and anilide. The former melted at 108°, the latter at 97·5°. Marie gave the melting point of the amide as 109°, Lipp and Kuhn* 106°, and the latter state that the anilide melts at 97°.

With neither of these derivatives were we able to effect any separation by either fractional crystallisation or saponification and, in all cases, the acid recovered melted at the same temperature as the original preparation.

The heats of crystallisation of some of the higher synthetic fatty acids are being investigated here by Prof. Garner, and Dr. King, who is carrying out this work, was kind enough to determine this constant for our preparation. A value of 52·25 cal. per gram was obtained, which indicates a carbon content of 18, provided that a straight chain acid is present. As such a content is entirely out of the question, this is the clearest possible indication that cerotic acid is a mixture.

Source ii. Oxidation of Paraffin Wax.—Several specimens of acids, obtained from the oxidation of paraffin wax, very similar to cerotic, have been previously described (Acids, A, p. 233). We give a further illustration of a material from the same source which melted at 80°, acid value 141, C 79·1 per cent., H 13·3 per cent., and whose methyl ester melted at 62·5° (Specimen C).

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* 'J. Prak. Chem.,' vol. 86, p. 192.

Source iii. Oxidation of n-triacontane.—The specimen from the oxidation of synthetic triacontane has been previously described, see p. 231. The ethyl ester melted at 60·5° (Specimen D).

Source iv. Carnauba Wax.—Miss Bickle isolated the acids and alcohols from carnauba wax in these laboratories; the former, after purification, melted at 78°. The impure acids were then converted into their ethyl esters which boiled between 220° and 240° at 3 mm. By a combination of recrystallisation and fractionation *in vacuo*, the three specimens F, G, and H were obtained. The analysis of the first and last are given below.

		C.	H.	Calculated.
		per cent.	per cent.	
F	Acid	78·4	13·3	$C_{26}H_{52}O_2$: C = 78·8 per cent.; H = 13·1 per cent.
	Ethyl ester	78·5	13·0	
H	Acid	78·6	12·9	$C_{28}H_{56}O_2$: C = 79·2 per cent.; H = 13·2 per cent.
	Ethyl ester	78·5	13·0	

These three specimens of acids appeared to us to correspond closely to those described by previous observers but other acids are present whose esters boil at a higher temperature and these will be investigated later.

Source v. Chinese Wax (i).—Mr. Tutin gave us two preparations of cerotic acid from Chinese wax which had been partly purified by the fractionation of their methyl esters. After several recrystallisations of the purer specimen, which melted at 78·5°, we found that the acid melted at 80·2° and its ethyl ester at 62·3°. Although these specimens appeared as pure as many others we had investigated, yet, when photographed, the resulting plates indicated clearly that this was not the case.

Chinese Wax (ii).—Mr. F. C. Lewis saponified a specimen of Chinese wax which was white, well crystalline, and melted at 81°, and this temperature was only raised to 82·5° on repeated recrystallisations. An X-ray photograph of the latter gave a reasonably good plate and a value of 72·0 Å.

On saponification, the resulting acid after several recrystallisations melted at 79·5° and gave an acid value of 140. This acid was converted into its ethyl ester, which melted at 62–63°, and fractionated in a vacuum of 0·2–0·5 mm.; finally, three fractions were obtained which, after crystallisation from alcohol, melted at (i) 59·5°; the main bulk (ii) 63°, (iii) 66·5–67°; residues. The acid

Table X.—Cerotic Acid.

Specimen.	M.P.	Comparison M.P. extrapolated values.*	Spacings in Å.				Suggested composition of specimen of acid.
			Acid.	Comparison acid. See Table III.	Ethyl ester.	Comparison ethyl ester.	
Beeswax—							
A	78	$C_{24+25+26}$=79·4	68·03	B of C_{28}=68·2	39·15	C_{30}=39·2	26+28, latter predominating in A.
B	78·5	*C_{26+28} =83·7	67·0				
B_1	78·5	*C_{28} =91	67·85				
Paraffin wax—							
C	80		68·8				28 with shorter chain.
Triacontane—							
D	78		68·85		39·0		Same as A, etc.
E	84·5	*C_{28+30}=87·6	69·4				28 and probably some 30.
Carnauba wax—							
F	78	C_{24+26} =79·8	60·4	B of C_{24}=58·5	36·0	C_{28}=37·0	24+26.
G	76·5	*C_{26+27} =83·5	65·5	B of C_{26}=63·3	37·6	C_{29}=38·0	26+27 and shorter chain.
H	81	*C_{28+30} =87·6	71·85	B of C_{30}=73·0	40·5	C_{32}=41·6	28+30 and shorter chain.
Chinese wax—							
J	82·5	*C_{26+28} =83·7	63·2				26+28, former predominating.
K	85·5		63·5		39·3		

from ester (i), after purification, melted at 82·5° and gave an acid value of 136 (Specimen J). There is but little doubt that this material constitutes the main quantity of the acid present in combination in Chinese wax. The ester melting at 63°, (ii) gave an acid melting at 83°. From the ester melting at 66·5–67°, (iii) an acid melting at 85·5–86° was isolated, with an acid value of 128 (Specimen K).

Chinese Wax ?—A specimen of unknown origin was placed at our disposal by Prof. Garner. It had probably been obtained from Chinese wax. From this we obtained a small quantity of acid melting at 84·5° (Specimen E). The larger amount present melted at 81°.

The X-ray spacings of the cerotic acid from *beeswax* are close to that of an acid $C_{28}H_{56}O_2$, 68·2 Å., and judging from all the data, this acid is certainly mixed with $C_{26}H_{52}O_2$. The melting point of any specimen of ethyl ester over 60° is a clear indication of the presence of the ester of an acid of higher carbon content than 26.

The spacings of the acids from *carnauba wax* indicate the presence of acids with a carbon content from 24 to 30.

The acid from *Chinese wax* which is present in preponderating amount is $C_{26}H_{52}O_2$, which is mixed with smaller quantities of $C_{28}H_{56}O_2$, and we think it possible that the former could be isolated in a pure condition. Prof. Holde sent us a specimen isolated from Chinese wax, which melted at 87°, gave 62·7 Å. and 57·4 Å., and was clearly a pure preparation of $C_{26}H_{52}O_2$.

IV. *Montanic Acid.*

Montanic acid was supposed to be $C_{29}H_{58}O_2$ by von Boyen* and by Eisenreich.† Ryan, however, states that it is $C_{28}H_{56}O_2$.‡ Meyer and Brod§ consider that it is not the *n*-acid $C_{28}H_{56}O_2$. Wood and Nicholas‖ give the melting point as 84–85° and the acid value between 136 and 132. Holde, Bleyberg and Vohrer¶ showed the presence of several acids, chief among which is $C_{28}H_{56}O_2$, melting point 84·4° (montanic acid).

Prof. H. Ryan sent us specimens of montanic acid and its ethyl ester. The former was prepared from montana wax, said to have been obtained from peat.* He considered that the acid was $C_{28}H_{56}O_2$.

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* ‘Z. angew. Chem.,’ p. 1110 (1901).

† ‘Chem. Rev. Fett. u. Harz. Ind.,’ vol. 16, p. 211 (1909).

‡ ‘Proc. R. Irish Acad.,’ vol. 21, sec. B, No. 4, p. 95 (1913).

§ ‘Monat.,’ vol. 34, p. 1143 (1913).

‖ ‘J. Inst. Pet. Tech.,’ vol. 14, p. 493 (1924).

¶ ‘Brennstoff Chemie,’ vol. 6, pp. 102, 124 (1929).

The acid is stated to melt at 83·6°, acid value 131·6, and its ethyl ester melts at 64–65°. The specimens sent us, after recrystallisation, melted at 82·6° and the ethyl ester at 65°.

The spacing of the acid, calculated from a poor photograph, was 69·0 Å., and a better plate was not obtained after a further crystallisation. The photographs were a clear indication of impure material. The ethyl ester gave 43·9 Å.

It is possible that this acid is chiefly composed of a mixture of acids with a carbon content either of 28 and 30 or of 28, 30 and 32. We had insufficient quantity to test this question further. The B spacing of 30 is 73·0, and the C spacing 65·8 Å.; the ethyl ester of 34 is 43·3 Å.

A small quantity sent us by Prof. Holde melted at 88° and gave the spacings 67·6 Å. and 61·4 Å.; it certainly contained $C_{28}H_{56}O_2$, probably in preponderating amount, and possibly an acid of smaller carbon content.

V. *Cluytinic Acid.*

Mr. Tutin placed at our disposal two specimens of cluytinic acid which he had isolated from hops,† and from *Cluytia Similis*.‡ He believed that this acid melting at 69° was $C_{21}H_{42}O_2$. The former gave a spacing of 57·2 Å., the latter 55·1 Å. Clearly they were not identical. Morgan and Holmes (*loc. cit.*) had previously measured the spacings of the acid from the latter source and found 54·5 Å.

It is clear from these measurements that although cluytinic acid may contain an acid with a carbon content of 21, it is certainly a mixture. The spacing 57·2 Å. points to $C_{25}H_{50}O_2$, which is 57·7 Å.; and 55·1 Å. and 54·5 Å. may be a distortion of $C_{23}H_{26}O_2$ (53·4 Å.) due to the presence of higher acids. The melting point and ultimate analyses indicate admixture of acids with much lower carbon content.

The X-ray analyses of the acids from natural sources have shown that in all cases they are mixtures of *n*-fatty acids, which accounts for the divergence of their melting points from those of the pure synthetic acids to which they were supposed to correspond.

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* 'Sci. Proc. Roy. Dublin Soc.,' vol. 12 (N.S.), p. 202 (1909); 'Proc. Roy. Irish Acad.,' vol. 30, Sec. B, p. 97 (1913).

† Power, Tutin, and Rogerson, 'J. Chem. Soc.,' p. 1267 (1913).

‡ Tutin and Clewer, 'J. Chem. Soc.,' vol. 101, p. 2222 (1912).

It is not surprising that those who have investigated these acids have experienced the difficulty—or even stated the impossibility—of effecting a separation by such a process as that of the fractionation of their esters. We have found that, by this method, fractions boiling over a small range could be obtained, and that in these, the proportions of the constituents vary as shown by the alteration of the spacings, but with the amounts at our disposal, we could not effect the separation of a pure constituent, although the isolation of *small amounts* of pure acids should be possible in certain cases, such as, for instance, hexadecanic acid from the acids of Chinese wax, in which it predominates.

It is unlikely that specimens of acids from natural sources, such as arachidic, cerotic, lignoceric and montanic, are always composed of the same mixture of acids in the same proportion. Small variations in these proportions mean but small alterations in the melting points of either the acids or their esters. On the other hand, it is possible that the acids obtained from such a material as beeswax should vary in their carbon content depending on the source of the wax. Prof. Holde sent us a "cerotic acid" melting at 84°, which gave spacings of 52·5 Å. melted, 53·0 Å. pressed, showing that it was a fairly pure specimen of $C_{24}H_{48}O_2$. A pure acid should also have shown the B spacing 58·5 Å. No trace of an acid of this low carbon content was present in our preparation. Considerations such as these might be taken in conjunction with the previous discussion, as accounting for the different formulæ which, from time to time, have been assigned to the above acids.

PART IV.—ALCOHOLS FROM CHINESE WAX AND CARNAUBA WAX.

A review of the literature on the higher alcohols combined as esters in the various waxes, shows—amongst those most studied—that ceryl alcohol melting at 79° has the lower, and melissic or myricyl alcohol, melting point between 85° and 88°, the higher carbon content. The actual content of these alcohols, however, which most probably belong to the *n*-fatty series, is generally considered to be 26 in the former and 30 in the latter. Ceryl alcohol on oxidation gives cerotic acid, which has been previously discussed, and the conclusions we have drawn as to the nature of the acid apply equally to the alcohol.

As regards melissic alcohol, Heiduschka and Gareis,* for instance, showed that this alcohol obtained from beeswax melted at 85·5° and gave an acid melting at 88·5°, whereas prepared from carnauba wax, it melted at 87·5°, and the acid at 90°. They also investigated a series of similar derivatives of the two alcohols and acids. They concluded that the former alcohol had a carbon content of 30 and the latter 31.

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* 'J. Prak. Chem.,' vol. 99, p. 293 (1919).

The literature on the alcohols, although these substances have not been examined to the same extent as the acids, shows an uncertainty as to their carbon content very similar to that already discussed. This uncertainty is increased since no direct comparison has yet been made with synthetic *n*-alcohols or with acids of a carbon content greater than 26.

We propose to investigate the nature of these alcohols, and now give a preliminary note on those obtained from Chinese and carnauba wax.

Chinese Wax.—The alcohols from Chinese wax were isolated by Mr. F. C. Lewis, and, after several recrystallisations, melted at 79°. They were converted into their acetic acid esters, which were fractionated in a vacuum of 0·2–0·5 mm. After carrying out this operation three times, two main fractions were obtained :—

Fraction i.—The acetate melted at 60°, giving an alcohol melting at 79° and an acid melting point 82° (Specimen A). The acid was prepared by oxidation of the alcohol in acetic acid solution by chromic acid. The yields were excellent. The ethyl ester of the acid melted at 60°. The acetate of an intermediate fraction melted at 62°, the alcohol at 80°.

Fraction ii.—The acetate melted at 65–66°, the alcohol at 83°, and the corresponding acid at 83°. The ester of this acid melted at 64·2° (Specimen B).

It is clear from the above that no separation had been effected by the process of fractional distillation, if indeed it is possible with the type of apparatus usually employed. The results of this fractionation indicated that we were dealing with a mixture of at least two substances, the lower amounting to about 80 per cent. and the higher 20 per cent.

Carnauba Wax.—Considerable quantities of the alcohols from this source had been prepared by Miss Bickle, and their further investigation was carried out by Mr. F. E. Heal. The recrystallised alcohols melting at 86–87° were converted into their acetic acid esters and these fractionated in a vacuum of 2·5 mm.

Fraction i.—Boiling point 275–280°. Acetate melting point 70°, alcohol 85·5°, acid 91·5°.

Fraction ii.—Boiling point 280–285°. Acetate melting point 71–72°, alcohol melting point 87–88°.

Fractions (i) and (ii) are very similar. Fraction (ii) was again fractionated in a vacuum of 1–2 mm., and the material boiling at 225° at 1·4 mm. gave an alcohol, melting point 87·3°. The alcohols from the first fraction were purified further and gave an acid melting at 92° (Specimen C), whose ethyl ester melted at 71·5°. An attempt was made to purify this acid by treating its potassium salt with various solvents, and, after this, the acid showed the same melting point, but that of the ester rose to 72·5° (Specimen D). It is probable that the ethyl ester of an acid with a carbon content of 30 would fuse at about 70°.

Fraction iii.—Boiling above 285°. Acetate 73·5°. alcohol 88–89°, acid 92° (Specimen E), ethyl ester 73·4°.

Table XI.—Acids from Higher Alcohols.

Specimen.	M.P. alcohol.	M.P. acid.	M.P. ethyl ester.	Spacings.		Suggested carbon content of specimen.
				Acid. Å.	Ester. Å.	
Chinese wax—						
A	79	82	60	57·8	34·7 39·2	Mixtures of 26 and 28.
B	83	83·8	64·2	69·3	41·3	28, with higher acid, probably 30.
Carnauba wax—						
C	87–8	93	71·5	76·7	45·0	Mixtures of acids, highest probably 34, whose spacing is 83·0 Å.; ethyl ester of 36 is 45·5 Å.; the lowest acid is probably 32, whose C spacing is 70·2 Å, ethyl ester of 34 is 44·5 Å.
D	87–8	92	72·5	78·0	46·1	
E	88–9	92	73·4	82·0	47·4	

Again, the range of the boiling point of the acetates showed that we were dealing with a mixture, although there was but little difference between the melting point of the various fractions of alcohols, esters and acids ; had it not been for the X-ray examination, the inference that a pure material had been isolated might easily have been made.

The results of this preliminary investigation of the alcohols in Chinese and carnauba waxes have shown that, in addition to those of the same carbon content as the acids with which they are combined, there are also present higher members of the same series. But we think it is clear that these alcohols, like the acids, are mixtures, and that, up to the present, pure materials have not been isolated. It follows that the various derivatives of "melissic" alcohol and acid described in the literature and which have been synthesised from such sources, are also mixtures.

Our thanks are due both to the Department of Scientific and Industrial Research for grants which enabled Drs. Christie, Jefferis, and Wallington to take part in the investigation described in Part II, and to the Colston Research Society for defraying part of the expenses of the work.

The Raman Spectra of some Aldehydes and of Mesitylene.

By S. Venkateswaran and S. Bhagavantam.

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1.—*Introduction.*

The results of a study of the Raman spectra of nine aldehydes and of mesitylene are reported and discussed in this paper. Of these substances, only a few, namely, paraldehyde, acetaldehyde and benzaldehyde have been previously investigated by other authors* and the rest receive attention for the first time.

The experimental arrangements were the same as those described by Wood.† Hilger's quartz E_2 and a two prism glass spectrograph of high light gathering power were used for studying the spectra. The liquids were mostly Kahlbaum's or Merck's extra pure and were further purified by distillation in vacuum before use. Capric, undecylic, and lauric aldehydes were, however, obtained from other sources and were used as received. In the following tables are given the wave-numbers and the intensities of the Raman lines, and the shifts in wave-numbers between them and the exciting lines. In the column $\Delta\nu$ the letters $a, b, c, d, e, f, g, h, k, l$ and m represent the exciting lines of the mercury spectrum λ A.U. 3650·1, 3654·8, 3663·3, 4046·6, 4077·8, 4339·2, 4347·5, 4358·3, 5460·7, 5769·5, 5790·5 respectively.

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* Petrikaln and Hochberg, 'Z. Phys. Chem.,' vol. 4, p. 299 (1929); Dadieu and Kohlrausch, 'Sitz. Ber. Wien Akad.,' vol. 138, pp. 419, 607 (1929).

† Wood, 'Phil. Mag.,' vol. 6, p. 729 (1928).

2. *Results.*

Acetaldehyde.—Kahlbaum's acetaldehyde was purified and freed from possible traces of paraldehyde by distillation in vacuum. The liquid was sealed off in a Wood's tube and the spectrum photographed immediately. The latter is found to exhibit, in addition to discrete lines, also a feeble continuous spectrum. Table I gives the analysis of the spectra.

Table I.*—Acetaldehyde, $CH_3\,.\,CHO$.

I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu$.
1	24462	*a* — 2927	0*b*	23278	*d* — 1427	1*d*	21594	*e* — 2922
1	24420	*a* — 2969	0	23101	*e* — 1415	1*d*	21519	*h* — 1419
1	24369	*b* — 2985	1	22418	*h* — 521	0	21289	*g* — 1706
0	24184	*d* — 521	0	22252	*h* — 686	2*b*	21211	*h* — 1727
0*b*	24014	*d* — 691	0*d*	22160	*h* — 778	0	20084	*h* — 2854
0*b*	23923	*d* — 782	0*d*	22040	*h* — 898	2	20022	*h* — 2916
0*b*	23794	*d* — 911	1*d*	21859	*d* — 2846	0	19942	*h* — 2996
0*b*	23568	*d* — 1137	6	21783	*d* — 2922			
0*b*	23435	*d* — 1270	0*d*	21706	*d* — 2999			

$\Delta\nu$: 521 (1); 688 (0); 780 (0*b*); 905 (0*b*); 1137 (0*b*); 1270 (0*b*); 1417 (1*b*); 1727 (2); 2850 (1); 2922 (5); 2997 (0).

Paraldehyde.—The continuous spectrum observed with this liquid is even more prominent than in acetaldehyde.

Table II.—Paraldehyde, $(CH_3\,.\,CHO)_3$.

I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu$.
0	24545	*a* — 2844	0	23600	*d* — 1105	0*b*	21850	*d* — 2855
3	24445	*a* — 2944	0*d*	23527	*d* — 1178	6	21761	*d* — 2944
2*b*	24408	*b* — 2946	0*d*	23463	*h* + 525	3*d*	21706	*d* — 2999
2*b*	24389	*a* — 3000	0*d*	23356	*d* — 1349	1*d*	21588	*h* — 1350
1	24353	*b* — 3001	1*d*	23251	*d* — 1454	1*d*	21562	*e* — 2954
1*b*	24291	*c* — 2999	2	22466	*h* — 472	1*d*	21483	*h* — 1455
1*d*	24233	*d* — 472	4*s*	22413	*h* — 525	0*d*	20054	*g* — 2941
3	24180	*d* — 525	0*d*	22103	*h* — 835	3	19993	*h* — 2945
0	23970	*d* — 735						
0	23929	*d* — 776	0	22039	*h* — 900	1*b*	19935	*h* — 3003
1*b*	23860	*d* — 845	0	21976	*h* — 962	0	17773	*k* — 535
0*d*	23805	*d* — 900	0	21913	*h* — 1025			

$\Delta\nu$: 472 (2); 525 (4); 735 (0); 776 (0); 840 (1); 900 (0); 962 (0); 1025 (0); 1105 (0); 1178 (0); 1350 (1); 1455 (1); 2850 (0); 2945 (5); 3000 (2*b*).

* The following abbreviations are used in the tables :—

I = intensity ; ν = wave-number of the Raman line ; $\Delta\nu$ = shift in wave-numbers ; *b* = broad, *d* = diffuse ; *s* = sharp.

Benzaldehyde.—The modified lines of wave-lengths lower than λ 4358·3 appear distinctly weaker in comparison with the corresponding lines appearing lower down the spectrum. This is evidently due to the absorption of the liquid in the former region.

Table III.—Benzaldehyde, $C_6H_5 . CHO$.

I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu$.
0	23706	*d* — 999	0	22190	*h* — 748	0	21479	*h* — 1459
0	23537	*d* — 1168	2	22109	*h* — 829	0	21445	*e* — 3071
0	23500	*d* — 1205	8	21937	*h* — 1001	0	21397	*g* — 1598
2	23107	*d* — 1598	1	21915	*h* — 1023	8	21341	*h* — 1597
1*d*	22800	*e* — 1716	3	21770	*h* — 1168	1*d*	21284	*g* — 1711
0*b*	22690	*h* — 248	8	21734	*h* — 1204	8	21237	*h* — 1701
1	22497	*h* — 441	0	21706	*h* — 1232	1	19870	*h* — 3068
2	22321	*h* — 617	3	21639	*d* — 3066			
0	22287	*h* — 651	0	21541	*h* — 1397			

$\Delta\nu$: 248 (0); 441 (1); 617 (2); 651 (0); 748 (0); 829 (2); 1000 (6); 1023 (1); 1168 (3); 1205 (6); 1232 (0); 1397 (0); 1459 (0); 1598 (7); 1701 (7); 3068 (3).

Anisaldehyde.—This liquid also shows marked absorption in the violet, the Raman lines falling in this region of the spectrum being consequently very weak.

Table IV.—Anisaldehyde, $CH_3O . C_6H_4 . CHO$.

I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu$.
0	23543	*d* — 1162	0	21888	*h* — 1050	0	21468	*h* — 1470
0	23123	*d* — 1582	10	21776	*h* — 1162 *d* — 2929	0	21431	*f* — 1608
2*d*	23104	*d* — 1601				0	21388	*g* — 1607
1	22331	*h* — 607	4	21724	*d* — 2984	8*s*	21358	*h* — 1580
1	22293	*h* — 645	2	21674	*d* — 3031	10	21336	*h* — 1602
0	22169	*h* — 769	2*d*	21625	*d* — 3080	10*b*	21251	*h* — 1687
0	22144	*h* — 794	0	21597	*e* — 2919	0	20014	*h* — 2924
2	22101	*h* — 837	0	21570	*g* — 1425	0	19922	*h* — 3016
2	22079	*h* — 859	0	21538	*h* — 1400	0	19862	*h* — 3076
0	21929	*h* — 1009	3	21509	*h* — 1429			

$\Delta\nu$: 607 (1); 645 (1); 769 (0); 794 (0); 837 (2); 859 (2); 1009 (0); 1050 (0); 1162 (2); 1400 (0); 1429 (3); 1470 (0); 1580 (6); 1602 (7); 1687 (7); 2924 (5); 2984 (4); 3024 (2); 3078 (2).

Salicylaldehyde.—The liquid was coloured slightly yellow.

Table V.—Salicylaldehyde, OH . C_6H_4 . CHO.

I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu$.
0	22780	*h* — 158	2	22170	*h* — 768	2	21476	*h* — 1462
0	22676	*h* — 262	1	21909	*h* — 1029	1	21357	*h* — 1581
1	22481	*h* — 457	1	21786	*h* — 1152	2*d*	21275	*h* — 1663
1	22373	*h* — 565	2	21708	*h* — 1230			
0	22277	*h* — 661	1	21612	*d* — 3093			

$\Delta\nu$: 158 (0); 262 (0); 457 (1); 565 (1); 661 (0); 768 (2); 1029 (1); 1152 (1); 1230 (2); 1462 (2); 1581 (1); 1663 (2*d*); 3093 (1).

Cinnamic Aldehyde.—Two photographs were taken with this liquid, one using Ilford Isozenith plate for the violet and blue regions, and the other with panchromatic plate for the longer wave-length region.

Table VI.—Cinnamic Aldehyde, C_6H_5 . CH : CH . CHO.

I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu$.
0	25990	*a* — 1399	3	21548	*h* — 1390	6	17183	*k* — 1124
1	22330	*h* — 608	0	21498	*h* — 1440	0*d*	17120	*k* — 1187
1	22097	*h* — 841	1	21443	*f* — 1596	7	16969	*k* — 1338
5	21939	*h* — 999	0	21404	*g* — 1591	0	16915	*k* — 1392
0	21863	*g* — 1132	10	21329	*h* — 1609	7	16704	*k* — 1603
5	21814	*h* — 1124	8	21266	*h* — 1672	5*d*	16631	*k* — 1676
4	21758	*h* — 1180 *d* — 2947	0*d*	17696	*k* — 611	0	15730	*l* — 1598
6	21689	*d* — 3016				0	15646	*m* — 1619
3	21612	*d* — 3093 *h* — 1326				0*d*	15585	*m* — 1680

$\Delta\nu$: 610 (1); 841 (1); 999 (5); 1124 (6); 1183 (1); 1332 (5); 1391 (2); 1440 (0); 1603 (8); 1676 (7); 2947 (3); 3016 (6); 3093 (3).

Capric, Undecylic and Lauric Aldehydes.—These liquids were studied without any special purification. They all showed a strong continuous spectrum against which only two prominent frequency shifts corresponding to 3·5 μ and 5·7 μ respectively could be definitely measured. The shift of 3·5 μ gives a very broad band without any structure. In this respect it is in striking contrast with the appearance of the same band in the spectra of the earlier members, *e.g.*, acetaldehyde, where it is distinctly resolved into three equally spaced lines, the central one being the most intense. A similar tendency of this band to diffuseness as we go to the higher members of a homologous series has been observed also in the case of paraffins, alcohols and fatty acids.*

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* Ganesan and Venkateswaran, 'Ind. J. Phys.,' vol. 4, p. 195 (1929).

3. *Discussion of the Results.*

It may not be out of place here to make a remark regarding the continuous spectrum observed in light scattering. That even the most carefully purified liquids persist in showing a distinct though very feeble, continuous spectrum has already been pointed out by one of us elsewhere* ; as also its tendency to get more prominent when we go to the higher members of a series probably due to the increasing viscosity of the liquids or to the increasing mass of the molecules. The origin of this continuous spectrum has not, however, been definitely understood. It may be mentioned here that the continuous spectrum appearing in the light scattered by paraldehyde is conspicuous as contrasted with that present in the light scattered by acetaldehyde.

The Raman frequencies for the various aldehydes, benzene, and mesitylene are represented diagrammatically in figure 1 for convenience. Before proceeding to discuss those characteristic of the aldehydes, we may first consider the frequency shifts for which the origin is already known. Thus, for example, the band at about 3·3 μ which appears in the scattered spectra of all the aliphatic hydrocarbons has been attributed to the C-H bond, and it may be seen from the figure that this continues to appear in paraldehyde and acetaldehyde which are characterised by such a linkage. Where the carbon atom forms part of a benzene ring, as, for example, benzaldehyde, cinnamic

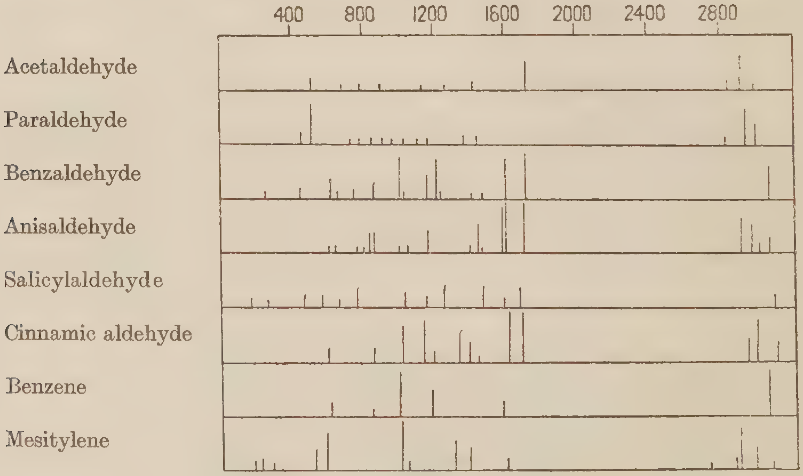

Fig. 1.

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* Venkateswaran, 'Ind. J. Phys.,' vol. 3, p. 105 (1928) ; see also Venkateswaran, 'Phil. Mag.,' vol. 7, p. 597 (1929).

aldehyde or salicylaldehyde, the band appears in a slightly shifted position which again is characteristic of the latter type of C-H bond. In anisaldehyde the presence of both these types of bonds is seen to result in the occurrence of Raman lines characteristic of both.

A comparison of the Raman spectra of benzene and the four aromatic aldehydes studied in this paper, reveals some interesting relationships. It may first be remarked that the vibrational frequencies characteristic of the benzene molecule continue to appear in all the above four compounds in more or less the same positions, a result which might be expected from the fact that they all contain the benzene nucleus. That this is mostly true of all the aromatic compounds containing the benzene nucleus is borne out by the extensive study made, so far, of their Raman spectra by various investigators.

While this is no doubt generally true it must, however, be remembered that in the various derivatives of benzene the ring structure is subjected to different kinds of strain resulting from different modes of substitution of atoms or atomic groups of widely varying masses. It is hardly conceivable that such increasing complexity in the structure will leave the nuclear vibrations unaffected. Further, as a result of such transformations one might expect the system to develop a larger number of fundamental oscillations. This latter conclusion is, no doubt, in good agreement with the observed phenomenon, namely, that a derivative of benzene has always a much larger number of Raman frequencies than benzene itself, which presumably represent its fundamental modes of oscillation. As stated above, in the derivatives those frequencies that are characteristic of benzene also appear, surprisingly, however, in more or less the same positions, the prominence with which they appear varying widely from compound to compound. This variation is particularly conspicuous in the case of the Raman line corresponding to $\Delta\nu$ 993 occurring in this class of compounds and hence a detailed discussion of its behaviour with reference to the four aromatic aldehydes studied will now be made. For convenience and generality of the conclusions drawn, data regarding this particular frequency in the benzene derivatives studied by various other investigators will also be discussed here. It is seen from fig. 1 that this frequency ($\Delta\nu$ 993) is quite prominent in benzaldehyde and cinnamic aldehyde although not so striking as in benzene itself, whereas in anisaldehyde it is very feeble and salicylaldehyde does not show it at all. The latter two aldehydes belong to the class of di-substituted derivatives whereas the former two are mono-substituted ones which suggests at once that with increasing substitution this frequency becomes feebler and feebler. It is also of interest to note that the average value of this frequency in these aldehydes is about 1003 whereas the one in benzene is only about 993.* There is thus a distinct though small increase in this frequency on substitution amounting to about 10 wave-numbers. Besides this it will be seen that three of the aldehydes give a new frequency of about 1025 which is very close to the above one. That the above statements are very widely true is seen at once from the following table where the necessary data are collected.†

Table VII.‡

Substance.	ν_1.	ν_2.	Substance.	ν_1.	ν_2.	Substance.	ν_1.	ν_2.
Benzene	993		Cinnamic aldehyde	999	—	P-dichlorbenzene	—	1070
Nitrobenzene	1011	—	Salicylaldehyde	—	1029	Benzyl alcohol	1000	—
Orthonitrotoluene	—	1041	Anisaldehyde	1009	1050	Dimethyl aniline	992	1030
Toluene	1005	1029	Chlorobenzene	1004	1023	Benzonitrile	999	—
Orthoxylene	1000	1052	Bromobenzene	1002	1026	Benzyl chloride	999	1030
Meta-xylene	1000	—	Iodobenzene	998	—	Benzoyl chloride	1003	1028
Para-xylene	1009	1029	Phenol	1000	1018	Benzophenone	995	1022
Ethylbenzene	1005	1031	Acetophenone	993	1017	Benzyl nitrile	1008	—
Phenyl-methyl-ether	999	1023	Aniline	990	1018	Benzotrichloride	1001	1034
Benzaldehyde	1000	1023	O-dichlorbenzene	—	1037	Cyclohexane	992	1028

It is clear from the table that all the mono-substituted derivatives give the Raman line corresponding to $\Delta\nu$ 993 in benzene without any exception. Of the 10 di-substituted derivatives given in the table it appears very feebly in five of them whereas it has not been detected so far in the others. In all cases except one or two the frequency is, however, uniformly higher than in benzene, the average of all the values being equal to 1002. Further, practically every substituted compound gives the new Raman frequency the average value of which is about 1030.

The significance of such a splitting is far from being clearly understood especially in view of the fact that the values are not appreciably or only slightly affected by the nature of the substituent. In this connection it is, however, of great interest to draw attention to a similar phenomenon in the electronic band spectra of these molecules to which Mecke§ has drawn attention. In most cases the spectrum consists of six to eight strong bands with a frequency difference of about 930 which may evidently be identified with the principal vibration in the excited state. This corresponds to the fundamental vibration 993 in the normal state as revealed by the Raman spectra and infra-red absorption. Mecke suggests that the substitution of any atom or atomic group in the benzene ring results in an asymmetry which is accompanied by the development of two fundamental vibrations in the place of 920 of benzene itself. In the case of mono-derivatives of F, Cl, Br, CH_3 and C_2H_5 these asymmetric vibrations are represented by 930 and 965. With the substituent groups OH, OCH_3, NH_2, CN and CHO and in the case of di-substituted derivatives, the differences between these two principal vibrations (950 and 790 in the former and 1100 and 960 in the latter) are more marked.

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* Represents the mean value of those obtained by different investigators.

† See also Fujoka, 'Inst. Phys. Chem. Res. Japan,' vol. 11, p. 205 (1929).

‡ Data are collected mainly from papers by A. S. Ganesan and S. Venkateswaran; A. Dadieu and K. W. F. Kohlrausch; and A. Petrikaln and J. Hochberg.

§ Mecke, 'Handbuch d. Physik,' vol. 21, p. 552 (1929).

Although the above phenomenon is generally common to both Raman spectra and the electronic band spectra, and presumably has a similar origin, the fact must be emphasised that in our case the nature of the substituent group does not appear very seriously to affect the new fundamental frequency of about $\Delta\nu$ 1030, as is evidenced from Table VII. The fact, however, that both the frequencies are higher than the 993 characteristic of benzene does not seem to favour a quasi-mechanical explanation of the effect as due to an unsymmetrical loading of the benzene molecule by the substituent group.

It has already been mentioned that the intensity of the line corresponding to 993 in the Raman spectra diminishes rapidly with increasing substitution. The discussion so far has been restricted to mono- and di-substituted benzene derivatives, and at this stage it will, no doubt, be of interest to consider cases of higher substitution. As, however, no tri-substituted benzene derivatives have so far been studied, mesitylene, a typical representative of this class, was investigated by the authors. The results are given in Table VIII.

From the above conclusion, one would expect the Raman line $\Delta\nu$ 993 to be still feebler in mesitylene than in the xylenes whereas the Raman line $\Delta\nu$ 1030 may be expected to disappear as the structure is presumably symmetrical. Contrary to this, however, $\Delta\nu$ 993 is surprisingly strong comparable in intensity with that in benzene and $\Delta\nu$ 1030 also *does* appear although very feebly. This, no doubt, points to a close similarity between benzene and mesitylene which is evidently connected with the symmetrical ring structure common to both of them. That this frequency is undoubtedly the outcome of a six-membered carbon ring finds further support in that it appears in cyclohexane also.* The fact that Raman line $\Delta\nu$ 1030 appears in mesitylene and also in cyclohexane, especially in the latter, does not seem easy to reconcile with Mecke's idea of unsymmetrical loading.

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* Ganesan and Venkateswaran, *loc. cit.*

Table VIII.—Mesitylene, $C_6H_3(CH_3)_3$.

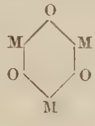
I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu$.	I.	ν_1.	$\Delta\nu_1$.
3*b*	24472	*a* − 2917	0	23210	*e* − 1306	2*b*	21685	*d* − 3020
		d − 233	0	23093	*d* − 1612	3*s*	21637	*h* − 1301
								d − 3068
3*b*	24432	*b* − 2922	0	22756	*h* − 182	0*d*	21599	*e* − 2917
		d − 273	1*d*	22705	*h* − 233	3	21557	*h* − 1381
3*b*	24372	*a* − 3017	0	22663	*h* − 275	0*b*	21501	*e* − 3015
0	24283	*e* − 233	4*s*	22417	*h* − 521	2	21328	*h* − 1610
		b − 3071						
2	24188	*d* − 517	8*s*	22362	*h* − 576	0	20209	*h* − 2729
4	24129	*d* − 579	0	22056	*f* − 982	3*b*	20072	*h* − 2866
0	23938	*e* − 578	0	22007	*g* − 988	6*b*	20026	*h* − 2912
		h + 1000						
8	23708	*d* − 997	0	21973	*d* − 2732	1*b*	19931	*h* − 3007
0*b*	23671	*d* − 1034	8*s*	21940	*h* − 998	1	18075	*k* − 233
1	23518	*e* − 998	0	21901	*h* − 1037	0	17790	*k* − 518
3	23404	*d* − 1301	1*d*	21837	*d* − 2868			
2	23327	*d* − 1378	8*d*	21786	*d* − 2919			

$\Delta\nu$: 182 (0); 233 (1); 275 (0); 519 (3); 578 (6); 998 (8); 1036 (0); 1301 (3); 1380 (3); 1611 (1); 2730 (0); 2867 (2*b*); 2917 (7*b*); 3015 (2*b*); 3069 (0).

Recent attempts to interpret the natural frequencies of a molecule in terms of different modes of oscillation of its component parts seem to show that, in general, each distinctive type of chemical linkage in the molecule gives rise to certain well-defined frequencies characteristic of it. Such calculations of the frequencies characteristic of any given type of linkage between two atoms have been made by several investigators based on their masses and their strength of binding. We may specially mention here the calculation by Dadieu and Kohlrausch (*loc. cit.*) who evaluate the latter quantity from the known constants of thermal dissociation for the given type of linkage. Thus

$$\nu = K\sqrt{\frac{A}{\mu}}, \tag{1}$$

where ν is the characteristic frequency, A is the constant of thermal dissociation, $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$, m_1 and m_2 being the masses of the two atoms and K is a constant which can be empirically determined from any one of such bonds. When A is expressed in kilo calories per molecule the numerical value of K has been calculated by the above authors to be 291·5.

We now proceed to discuss the different Raman frequencies given in the tables in relation to the structure of the molecules. The line corresponding to a shift of 1700 wave-numbers appears in the spectra of all the aldehydes studied here except paraldehyde, and is evidently due to the carbonyl group common to all of them. This is supported by the fact that the same line is conspicuous in the spectra of all the ketones, fatty acids, etc.,* which contain the group. That the line fails however to appear in the case of paraldehyde in spite of the C-O linkage present in it is not difficult to understand since the linkage of the carbon and oxygen atoms in this molecule is essentially different from that between the same atoms in the carbonyl group of the former class of compounds as is evidenced from the generally accepted formula for paraldehyde, viz., 

where M stands for the group ($CH . CH_3$). The carbon and the oxygen atoms are connected by a single bond as contrasted with the double bond between them in the carbonyl group. In support of this view, we may mention that the thermal dissociation constants for $C = O$ and C-O linkages are widely different.

If this view were correct, a calculation on the basis of formula (1) from the value 88 kilo calories per molecule for the dissociation constant of C-O gives 1045 for its characteristic frequency. This frequency actually appears not only in the spectrum of paraldehyde but also in other compounds containing this C-O linkage, *e.g.*, alcohols, fatty acids, ethers, etc., which have been studied for their Raman spectra.

An examination of the table of thermal constants, however, shows an appreciable difference in the values for the C-O linkage between the case where the carbon is aliphatic, and that where it forms part of a benzene ring, the actual values being 88 and 109 kilo calories per molecule respectively, in which case on the basis of formula (1) again we should expect compounds containing the aromatic C-O linkage to show a frequency equal to 1162. This is in conformity with observation, anisaldehyde giving a Raman frequency 1162 and salicylaldehyde 1152. Phenol and phenyl methyl ether also give 1178 and 1148 respectively.*

We next come to the $C = C$ linkage where both the carbon atoms have to be aliphatic. From the value of thermal dissociation energy for this linkage, viz., 125 kilo calories per molecule, ν_{C-C} comes out as 1330, which agrees surprisingly well with the frequency corresponding to one of the prominent Raman lines of ethylene (1342). Cinnamic aldehyde which has an ethylenic linkage has a frequency 1332 which also appears at practically the same positions in allyl alcohol (1332) and allyl chloride (1334).

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* Ganesan and Venkateswaran, *loc. cit.*

4. *Summary.*

All the nine aldehydes studied except paraldehyde exhibit in their Raman spectra a prominent line corresponding to a change in wave-number of about 1700. This frequency is therefore presumably characteristic of the $C = O$ linkage. The absence of this line in paraldehyde is intelligible as it does not contain $C = O$ in its structure.

A comparison of the results obtained with benzene and a large number of derivatives shows that the Raman line with a wave-number shift of 990 which is strong in benzene becomes weak in mono-substituted and still more weak in the di-substituted derivatives. Surprisingly, however, it again appears very prominently in mesitylene. Further, in practically all the derivatives this line is accompanied by a weaker Raman line at about $\Delta\nu$ 1030. Its relation to a similar phenomenon mentioned by Mecke in the electronic band spectra of these molecules is discussed.

The characteristic frequencies of certain groups are calculated on the basis of a method suggested by Dadieu and Kohlrausch. Good agreement is shown to exist between the calculated and the observed values.

In conclusion the authors desire to express their best thanks to Prof. Sir C. V. Raman and Mr. K. S. Krishnan for their kind interest in the work.

The Oxidation of Phosphine.

By R. H. Dalton, Ramsay Fellow.

(Communicated by C. N. Hinshelwood, F.R.S.—Received March 20, 1930.)

I. *Introduction.*

In a previous paper Hinshelwood* and the author described experiments on the oxidation of phosphine at low pressures in which it was shown that there is a limiting pressure below which the rate of reaction is negligibly slow but above which the mixture explodes. The results are satisfactorily accounted for if it is assumed that activation occurs by a chain mechanism and that the chains are broken principally on the walls. The present paper deals with the oxidation at higher pressures where there exists, as shown by Labillardière, van't Hoff, van der Stadt* and others, an upper limiting pressure above which the action is negligibly slow but below which the mixture explodes. Our results are for the most part in approximate agreement with theirs, but cover a wider variety of conditions. Since the present work was started there has appeared an elaborate paper on the same subject by Trautz and Gabler.† Our results differ from theirs in several important respects probably due to the fact that our gases were much drier. These differences will be presented in detail in the discussion of the results later.

Our procedure was in general to mix known quantities of oxygen and phosphine at liquid air temperature and, after warming to room temperature, expand until an explosion occurred as indicated by a bright flash. By cooling with liquid air we were able to avoid explosion during mixing even though working with dry gases. This enabled us to study the reaction under conditions of humidity which would have been difficult or impossible with other methods of investigation.

In the previous paper it was shown that the lower pressure limit depended on the tube diameter in such a way as to show that the reaction chains by which the oxidation proceeds were principally broken at the walls of the vessel. It is significant in connection with the general theory of chain reactions that the upper limit is subject to quite different conditions.

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* Dalton and Hinshelwood, 'Roy. Soc. Proc.,' A, vol. 125, p. 294 (1929); Labillardière, 'Ann. Chim. Phys.,' vol. 6, p. 304 (1817); van't Hoff, "Etudes de Dynamique Chimique"; van der Stadt, 'Z. physikal. Chem.,' vol. 12, p. 322 (1893).

† 'Z. Anorg. Chem.,' vol. 180, p. 321 (1929).

In investigating the effect of the tube diameter, of the nature of the walls, and of the addition of inert gases it is now found that the walls do not play an important part in determining the higher pressure limit. It must therefore be governed by deactivation of the reaction chains in the gas. If, moreover, we assume that deactivation occurs when one of the activated bodies by which the chain is propagated, strikes both an oxygen and a third body it is possible to account quite satisfactorily for the experimental results.

II. *Experimental Procedure.*

For the preparation of the materials the previous paper may be consulted. The apparatus differs somewhat from that used before and is shown in fig. 1. The gases were contained in reservoirs provided with manometers (not shown in the sketch). The reaction vessel R and connecting tubes were first evacuated, then the three-way capillary tap A was turned to connect R with the gas

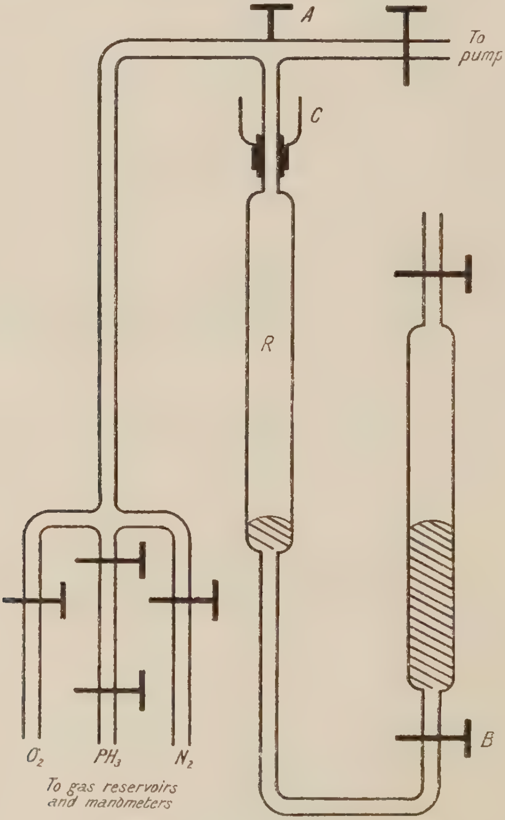

FIG. 1.

reservoirs and phosphine was admitted at a measured pressure. All pressure readings were made on the manometer at the gas reservoirs, time being allowed for equalisation of pressure between the reservoirs and R. A was now turned to close off R and at the same time to evacuate the connecting tubes. A small quantity of liquid air was placed in the cup C and after the phosphine had condensed, the oxygen was admitted at a known pressure. This freezing-out procedure was proved necessary by preliminary experiments in which attempts to mix the gases directly at high pressures always resulted in immediate explosion. The mercury in R, which during the admission of the gases was set at a point about the middle of the vessel to diminish the cooling correction, was now raised almost to the level of the liquid air cup so that when the liquid air had evaporated the gases were contained in a small volume at high pressures. When all parts of the tube had returned to room temperature the mercury was gradually withdrawn. At the moment of explosion, as shown by a flash, the tap B was closed and the position of the mercury in the reservoir noted. From this reading and the initial pressures and volumes, the pressure at the moment of explosion was calculated. The initial oxygen pressure was, of course, corrected for the effect of the cooling by liquid air. In experiments with the inert gas, the latter was added, after the oxygen, by pumping out the oxygen from the connecting tubes, letting in the inert gas at pressures above that of the oxygen and finally opening A. The connecting tubes and tap A were of small bore, and it was assumed that none of the oxygen diffused back during the admission of the inert gas, and that the pressure of the latter was its pressure in the reservoir less the oxygen pressure, taking account again of the effect of cooling.

To keep conditions as comparable as possible to those of the low pressure work the mercury in R was covered with a similar layer of phosphoric acid, although it was found later that its presence made very little difference at these pressures. The reaction vessel was surrounded by a water jacket to provide a means of keeping the temperature constant.

III. *Dependence of Explosion on Oxygen and Phosphine Pressures.*

The values of the phosphine and oxygen pressures (in millimetres of mercury) at which explosion occurred are given in Table I and are shown graphically in figs. 2 and 3.

Fig. 2A is a graph of series A made with a tube 1 cm. in diameter. It is apparent that when oxygen is in large excess the mixture will not explode until expanded to very low pressures. As the proportion of phosphine is increased

Table I.—T = 15° to 17° C.

Series A. (With H_3PO_4) Diameter 1 cm.		Series B. (With H_3PO_4) Diameter 0·4 cm.		Series C. (With H_3PO_4) Diameter 1 cm.	
p_{O_2}.	p_{PH_3}. (mm.)	p_{O_2}.	p_{PH_3}. (mm.)	p_{O_2}.	p_{PH_3}. (mm.)
97	284	79	287	29·6	7·4
87	228	84	281	25·2	4·4
84	198	78	173	20·2	2·9
81	121	73	167	19·4	2·6
75	101	84	116	16·6	2·1
75	85	74	100	14·8	1·8
73	79	83	88		
73	65	84	87		
69	58	79	85		
65	57	64	77		
64	54	65	77		
62	37	68	57		
55	23	66	57		
51	22	65	55		
43	13	63	55		
43	12	63	55		
42	12	68	54		
41	11	75	53		
41	9	75	51		
39	11	63	51		
36	8	60	50		
36	8	60	50		
34	7	57	48		
28	6	62	44		
27	4	59	41		
		63	35		
		40	14		
		41	14		
		48	12		
		36	7		
		31	6		
		31	6		
		27	5		
		25	4		

Values of the ratio p_{PH_3} to p_{O_2} for experiments in which no explosion occurred

0·06
0·07
0·09
0·09

Lowest value of the ratio for which an explosion was observed 0·12.

the pressures at explosion become rapidly higher until, in the neighbourhood of the point where oxygen and phosphine are present in equal proportion, the oxygen pressure begins to change more slowly and beyond this point becomes nearly constant. Fig. 3, made from series C and A, shows the relations at low pressures on a large scale. The lowest section of the curve is taken from Table I, series C of the previous paper which was also for a tube of 1 cm. diameter. As in the case of the low pressure work it was found that for very low values of the ratio of phosphine to oxygen no explosion occurred at any pressure. The curve comes very close to the oxygen axis but does not actually touch it. Some values of the ratio for which no explosion occurred are

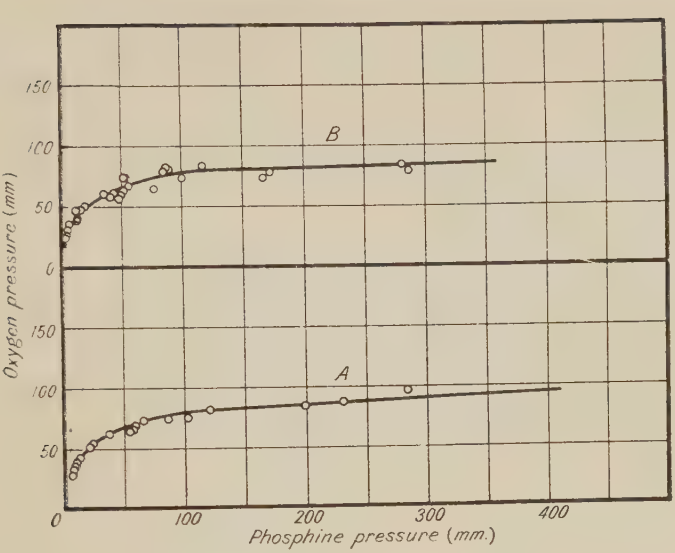
Oxygen pressure (mm)
150
100
50
0
150
100
50
B
A
0
100
200
300
400
Phosphine pressure (mm.)

FIG. 2.

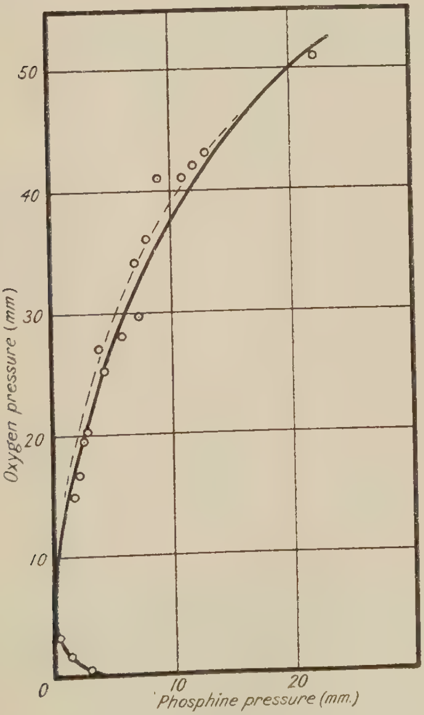
Oxygen pressure (mm)
50
40
30
20
10
0
10
20
Phosphine pressure (mm.)

FIG. 3.

given in Table I at the end of series C. The lowest value of the ratio for which explosion occurs is 0·12. Hence the limiting value lies between 0·09 and 0·12. This is in fair agreement with the value of about 0·1 obtained with a 1 cm. tube working from the low pressure side. It will, of course, vary with the diameter of the tube since the effect is caused by the appearance of wall deactivation as an important factor.

The values of series B, Table I, were obtained with a tube 0·4 cm. in diameter and are plotted in fig. 2B. The points are more scattered than in the case of the 1 cm. tube but the average curve is very nearly the same, showing that at the upper limit the tube diameter is not an important factor, *i.e.*, that the surface plays practically no rôle. The scattering of the points can be attributed partly to the fact that they were not taken in a single run but were obtained with two different tubes, the measurements extending over a considerable time. New tubes showed in general somewhat higher explosion pressures than used ones, probably due to some effect of the accumulating reaction product.

IV. *Influence of Surface and Temperature.*

To ascertain further whether the nature of the surface was an important factor a series of experiments were conducted in the absence of phosphoric acid. The results are given in Table II, series A.

Table II.

Series A. (No H_3PO_4) Diameter 0·4 cm.		Series B. (No H_3PO_4) Diameter 0·4 cm.		
p_{PH_3}.	p_{O_2}.	° C.	p_{PH_3}.	p_{O_2}.
4	33	15	133	80
101	74	15	118	78
118	78	15	101	74
133	80	20	130	75
173	92	20	135	78
186	66	31	174	127
194	68	31	186	116
222	73	40	540	293

While the values are perhaps less concordant than those in the presence of phosphoric acid the mean is nearly the same, again showing that the nature of the surface has little if any influence. This is in accord with the fact that the diameter of the tube was unimportant. The effect of temperature is shown in Table II, B. These measurements were also made in a tube with no phosphoric acid to avoid spurious effects due to escape of dissolved gases or change of the water vapour pressure caused by warming of the acid. It is clear from the table that the mixture becomes much more explosive at higher temperature. The effect, however, is a small one below 25°. Thus for the purpose of our experiments accurate temperature control was not necessary. In all of the experiments, except those given above, the temperature was kept between 15° and 17° C. by means of the water jacket around R.

V. *Influence of an Inert Gas.*

To obtain further information about the mechanism of the reaction the effect of adding an inert gas was studied. The data are given in Table III and plotted in fig. 4. Curve A is for series A with nitrogen and curve C for series C with argon.

Table III.

Series A. Nitrogen. Diameter 0·4 cm. $[PH_3]/[O_2] = 1·18$.		Series B. Nitrogen. Diameter 0·4 cm. $[PH_3]/[O_2] = 0·87$.		Series C. Argon. Diameter 0·4 cm. $[PH_3]/[O_2] = 0·85$.			
p_{O_2}.	p_{N_2}.	p_{O_2}	p_{N_2}.	p_{O_2}.	p_A.	p_{O_2}.	p_A.
65	0	63	0	57	0	68	0
64	0	43	41	60	0	49	54
44	50	32	59	63	0	43	61
29	83	26	64	60	0	49	54
23	94			66	0	39	91
21	104			63	0	38	113

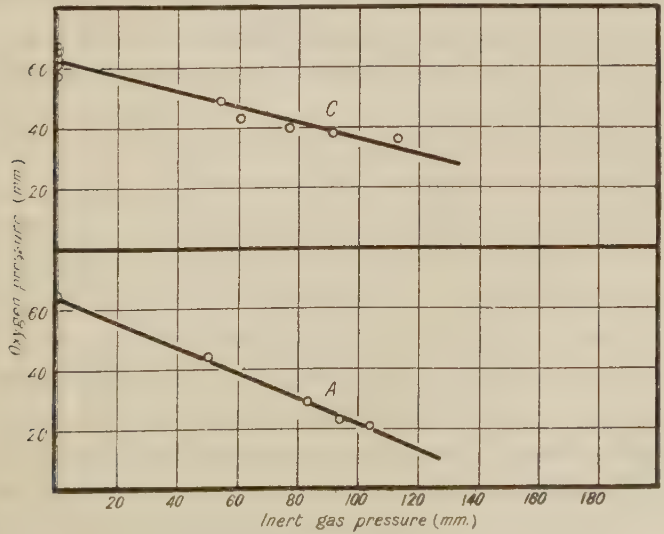

Fig. 4.

In making the measurements, the ratio of phosphine to oxygen was kept as constant as possible. In the curves the pressure of oxygen is plotted against the pressure of the inert gas. It will be noted that the inert gas makes the mixture less explosive which is just the opposite of what is expected if the walls are an important deactivating agent. Thus we have further proof that the action at the walls is unimportant. The decrease in the explosion pressure observed must be due to a deactivating action by the inert gas. In support of this it will be noticed that nitrogen exerts more influence than argon.

VI. *Rate of Reaction above the Explosion Limit.*

To discover if there was an appreciable reaction above the explosion limit a mixture of phosphine and oxygen was allowed to stand in R with tap B open so that any decrease of pressure would cause a movement of the mercury in the reservoir. No appreciable change was observed after 4 hours. Several days later the mixture was expanded. It exploded at approximately the predicted position assuming no reaction had taken place. After explosion the pressure fell to an inappreciable fraction of its original value. Hence above the critical pressure the reaction is immeasurably slow at room temperature. This is in agreement with the observations of van der Stadt who found the reaction to be quite slow even at 50° C.

VII. *Discussion of the Results.*

From the preceding results it is apparent that at the upper limit we are dealing with a phenomenon quite different from that prevailing at the lower limit. At low pressures there was a symmetrical relation roughly of the form $p_{O_2}\, p_{PH_3} = \text{constant}/d^2$ between the oxygen and the phosphine pressures when explosion occurred. Here d stands for the diameter of the cylindrical reaction vessel. On the other hand, at high pressures the relation is quite unsymmetrical and, in addition, is practically independent of the tube diameter. These results, together with the fact that at the upper limit the nature of the walls has little influence, and that the addition of an inert gas decreases, rather than increases the explosiveness, shows that the deactivating process in this case takes place in the gas phase rather than at the walls.

The form of the curve indicates that oxygen is principally responsible for the deactivation, in fact as the phosphine is increased the oxygen seems to approach a limiting value above which explosion cannot take place no matter how great the phosphine pressure. This was the conclusion reached by van der Stadt (*loc. cit.*) who found for the critical oxygen pressure with dry gases at 10° C.

a value of 0·1 atmosphere. He found, however, contrary to our observations that the oxygen pressure remained constant even at the lowest pressure of phosphine that he tried, which was about 20 mm. His procedure was, however, a rather difficult one to carry out and his observations were based on comparatively few experiments.

It is interesting to compare our results with those recently published by Trautz and Gabler (*loc. cit.*). They plotted the mole fraction of oxygen against the total pressure at explosion and found that with very moist gases this pressure passed through a maximum for a certain value of the oxygen. As the mole fraction of oxygen was increased beyond this point the pressure fell rapidly and the mixture became unexplosive at much lower oxygen ratios than was the case in our experiments. They also observed that it was possible to over step the explosion pressure (Überschreitungserscheinung) by rapid expansion, and then to obtain explosion by compressing, a phenomenon entirely unencountered in our work. With less humid gases they obtained results more closely approaching ours, but their procedure did not permit them to work with very dry gases. There are no experiments under comparable conditions. However, all the evidence indicates that the differences can be attributed to water vapour. Further experiments on the effect of water vapour would be very interesting.

Both sets of experiments lead to the conclusion that the nature of the walls is unimportant and that inert gases have a deactivating influence.

VIII. *Theory of the Upper Limit.*

The general methods used here will be the same as those used in developing the theory of the lower limit,* the principal difference being that wall deactivation will be assumed negligible, and gas deactivation introduced in its place.

As before, we will not concern ourselves with the origin of the first centres which give rise to chains, but only with the conditions affecting the rate of branching and the rate of deactivation of the chains, which are the important factors in the explosion phenomenon. The condition for explosion may be formulated in several ways, all of which lead to the same mathematical expression for the explosion limit. The explosion occurs when the pressures are such that the rate of production of new chains by branching just exceeds the rate of termination of chains by deactivation. Once this point is reached the number of chains increases exponentially with great rapidity and the reaction attains explosive velocity. The simplest derivation of the condition for explosion is obtained from the direct use of this relation. The limit may also be regarded, however, as the point at which each chain produces on the average one branch or as the point where the concentration of the active substance can no longer remain constant with time.

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* Dalton and Hinshelwood, *loc. cit.*

Let it be supposed that there are a certain number of active molecules, X_0 which react with phosphine giving an active product X_p and that this in turn reacts with oxygen, regenerating X_0 and so on until the chain is broken. It is evident that oxygen plays the principal rôle in the deactivation process in the gas phase : to account, however, for the precise form of the curves in figs. 2 and 3 a rather special assumption seems to be required. This is only obvious after rather detailed consideration, but for brevity it will be introduced at once. We will in fact assume that the breaking of the chains occurs whenever the active substance X_0 collides both with an oxygen and with some other molecule, that is, a second oxygen, a phosphine, or an inert gas molecule. As before, the possibility of branching will be introduced by assuming that collisions of X_0 with PH_3 can occasionally give rise to more than one X_p. Then we have for the rate at which chains are branching, $k\,[X_0]\,[PH_3]$, and for the rate at which chains are being broken

$$k_1\,[X_0]\,[O_2]^2 + k_2\,[X_0]\,[O_2]\,[PH_3] + k_3\,[X_0]\,[O_2]\,[N_2] + \dots,$$

assuming the inert gas nitrogen to be present. The k's are constants depending only on the nature of the substances and on the temperature. Equating the two rates and solving for $[PH_3]$ gives :—

$$[PH_3] = \frac{A\,[O_2]^2 + C\,[O_2]\,[N_2] + \dots}{1 - B\,[O_2]}, \tag{1}$$

as the condition for explosion, where

$$A = k_1/k, \quad B = k_2/k, \quad C = k_3/k.$$

To obtain an expression for the explosion limit from the condition that the number of branches per chain is equal to unity we start from the expression for the probability, W, that a given collision suffered by an X_0 molecule will result in its deactivation :

$$W = \frac{k_1\,[X_0]\,[O_2]^2 + k_2\,[X_0]\,[O_2]\,[PH_3] + k_3\,[X_0]\,[O_2]\,[N_2] + \dots}{\Sigma},$$

where Σ stands for the total number of collisions made by an X_0 molecule per second. But the average number of collisions of X_0 per chain, N, is $1/W$

since the chain must be of such a length that $WN = 1$. The probability that a given collision of an X_0 produces a branch is

$$\frac{k\,[PH_3]\,[X_0]}{\Sigma}.$$

Hence the condition that each chain produces on the average one branch is

$$\frac{k\,[PH_3]}{k_1\,[O_2]^2 + k\,[O_2]\,[PH_3] + k_3\,[O_2]\,[N_2]} = 1,$$

which gives equation (1) immediately.

Finally, we may obtain the condition for explosion by utilising the fact that $\partial\,[X_0]/\partial t$ must equal zero in order that a stable state prevail. We have

$$\frac{\partial\,[X_0]}{\partial\,t} = F + k_0\,[X_p]\,[O_2] - k_4\,[X_0]\,[PH_3] - k_1\,[X_0]\,[O_2]^2 \\ - k_2\,[X_0]\,[O_2]\,[PH_3] - k_3\,[X_0]\,[O_2]\,[N_2] = 0,$$

where F in some function giving the spontaneous rate of production of X_0, $k_0\,[X_p]\,[O_2]$ is the rate of production from X_p, and $k_4\,[X_0]\,[PH_3]$ is the rate of removal of X_0 to produce X_p. The partial differential is used to indicate that the volume is not varied so that only changes of X_0 due to reaction are considered. In virtue of the chain mechanism

$$(k_4 + k)\,[PH_3]\,[X_0] = k_0\,[X_p]\,[O_2].$$

Substituting this relation in the above equation we get

$$F + k\,[X_0]\,[PH_3] - k_1\,[X_0]\,[O_2]^2 - k_2\,[X_0]\,[O_2]\,[PH_3] - k_3\,[X_0]\,[O_2]\,[N_2] = 0$$

as the condition which must be satisfied if a steady state be possible. The only finite, positive values of $[X_0]$, $[PH_3]$, $[O_2]$, $[N_2]$ which satisfy the above equation are those for which

$$[PH_3] < \frac{k_1\,[O_2]^2 + k_3\,[O_2]\,[N_2]}{k - k_2\,[O_2]}.$$

Therefore the limiting condition is again

$$[PH_3] = \frac{A\,[O_2]^2 + C\,[O_2]\,[N_2]}{1 - B\,[O_2]}.$$

Putting in values of the constants determined from the experimental data we get for the case that no inert gas is present,

$$[PH_3] = \frac{4\cdot 3 \times 10^{-3}\,[O_2]^2}{1 - 9\cdot 1 \times 10^{-3}\,[O_2]}. \qquad (2)$$

The fact that constant B is roughly twice as great as A may indicate that nearly all three body collisions result in deactivation since the kinetic theory predicts that the coefficient for the frequency of collisions of the type B will be roughly twice that for the type A. The curve of equation (2) is practically indistinguishable from the curve A in fig. 2 and for this reason has not been separately drawn. The constants were determined from the central region of the curve (at phosphine pressures of 20 to 50 mm.) and the fact that extrapolation to very low and very high pressures gives results in such close agreement with observation is a satisfactory confirmation of the theory. The prediction of the theory at low pressures is shown by the dotted curve in fig. 3. Here again there is good agreement. At very low pressures the values of the phosphine pressure calculated for a given value of the oxygen are slightly smaller than those observed. This is to be expected since at low pressures wall deactivation, which has been neglected in the equation, will become prominent.

It is interesting that the mechanism assumed in the foregoing work is the only simple one which has been found to lead to anything approaching the experimental results. Trivial variations such as interchanging the rôles of X_0 and X_p, of course, produce no change in the conclusions, the essential points of the mechanism being the way the branching and deactivation depend on the oxygen, phosphine, and inert gas pressures. Any change in these assumptions leads to quite different results.

For the case that an inert gas is present, if the ratio of the oxygen pressure to phosphine pressure is constant as is the case in the experiments plotted in fig. 4 the theory predicts linear relation between the oxygen and the inert gas pressures, namely,

$$[\text{Inert gas}] = R/C - (0\cdot 43 + 0\cdot 91R)\,[O_2],$$

where R is the ratio $[PH_3]/[O_2]$.

Unfortunately the experiments in the presence of an inert gas are not very reproducible, but within the limit of the experimental error the curves are linear. At the highest inert gas pressures invesigated there is perhaps a tendency toward smaller effects than those predicted. From the slopes of the curves, C is found to have the value 10×10^{-3} for nitrogen and $5\cdot 3 \times 10^{-3}$ for argon. The fact that C for nitrogen has about the same value as B and about twice that of A may possibly indicate that all collisions of X_0 with an oxygen and a nitrogen molecule result in deactivation. The fact that this is not true in the case of argon is to be expected since the argon atom possesses fewer possibilities for taking up the energy of the active molecule.

Summary.

Mixtures of oxygen and phosphine are quite stable at high pressures even in the absence of moisture; but if the pressure is decreased a condition is reached at which the mixture explodes. The pressure at which explosion occurs is small for mixtures rich in oxygen, but increases rapidly at first and then more gradually as the proportion of phosphine is increased. The explosion pressure is independent of the dimensions of the vessel and the nature of its walls, but is decreased by the addition of an inert gas.

It is possible to account for the above results if we assume that the reaction occurs by a simple chain mechanism in which the chains are deactivated by three body collisions in the gas. The result obtained is

$$[PH_3] = \frac{4 \cdot 3 \times 10^{-3} [O_2]^2 + 10 \times 10^{-3} [O_2] [N_2]}{1 - 9 \cdot 1 \times 10^{-3} [O_2]}$$

where the bracketed expressions stand for the partial pressures of the gases indicated, and the constants are determined from the experimental data. If argon instead of nitrogen is used as an inert gas the coefficient of the last term of the numerator has the value $5 \cdot 3 \times 10^{-3}$.

The author wishes to express his most sincere thanks to Mr. C. N. Hinshelwood for suggesting and supervising this work which was carried out in his laboratory.

The Gyromagnetic Effect for Paramagnetic Substances.—I. *Description of Method and Results on Dysprosium Oxide.*

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In 1908, O. W. Richardson showed that if the magnetic properties of materials are due to the rotation of the electron orbits of the atom, a change U_l in the angular momentum should be accompanied by a change in magnetic moment M_l which is given by

$$U_l/M_l = 2m/e. \tag{1}$$

The angular momentum thus associated with the change of magnetic moment is very small, and has hitherto been measured only for ferromagnetic bodies. Experiments by various workers using different methods have shown that the angular momentum is within the limits of experimental error exactly one-half that expected on the orbital electron theory.* This has been known as the gyromagnetic anomaly. Recent theoretical developments, however, indicate that the source of magnetic moment in ferromagnetic bodies is due to the spin of the electron.† For the spinning electron, the relationship between change of magnetic moment and angular momentum is

$$U_s/M_s = m/e, \tag{2}$$

this equation being well established on the experimental side, principally from the Zeeman effect.

Evidence from various sources indicate that the magnetic moment in paramagnetic bodies arises from both spin and orbital contributions. In general, the proportionality of magnetic moment to angular momentum should indicate the relative proportions of spin and orbital magnetic moment, so that measurements of the gyromagnetic ratio for paramagnetic substances are desirable. The following is an account of the method evolved for such measurements and of results for one paramagnetic substance, dysprosium oxide.

As with ferromagnetic bodies there are two methods available. One can measure either (1) the change of magnetisation produced by rotation of the specimen, or (2) the angular momentum caused by change in magnetisation. The latter method seems capable of greater sensitivity, and is adopted in the present work. Two variations of this may be used, (*a*) the ballistic method, as used by Chattock and Bates and others, in which a single magnetising impulse causes a rotation of the specimen about its magnetic axis, or (*b*) the resonance method of Einstein and de Haas, later developed by the writer and others. In both methods one has to bear in mind that the substance used will probably be in powder form. In the former case, the mounting of this in the form of a cylindrical rod to obtain an appropriate magnetic moment necessitates a total weight of the specimen beyond the breaking strain of a suitable quartz fibre in order to obtain a measurable amplitude. Consequently the resonance method, where the frequency of the magnetising current is made equal to the natural period of oscillation of the suspended system, appears to be the only satisfactory one available.

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* See Chattock and Bates, 'Phil. Trans.,' A, vol. 223, p. 257 (1922), and Sucksmith and Bates, 'Roy. Soc. Proc.,' A, vol. 104, p. 499 (1923) for complete bibliography.

† Heisenberg, 'Z. Physik,' vol. 49, p. 619 (1928), has used the conception of the spinning electron to evolve a theory of ferromagnetism.

The amplitude produced at resonance by an alternating magnetising field $\mathrm{H}\cos\omega t$ is given by

$$\theta_r = \mathrm{K}m\chi\mathrm{HT}/\mathrm{I}\lambda, \tag{3}$$

where m = mass of paramagnetic substance used, χ = its mass susceptibility, T = time of oscillation, λ = logarithmic decrement, I = moment of inertia of the suspended system, and K is a numerical constant.

In view of the small value of χ for paramagnetic substances it is not possible to make θ_r large enough to be measurable unless the magnitudes of the other quantities in this equation are carefully chosen. In fact, the design of the apparatus depends almost exclusively upon the practicable limitations imposed upon the experimenter in making m/I, T, and I/λ as large as possible. This will be made evident in the description of the apparatus given below.

The substance chosen must be strongly paramagnetic and should follow the Curie law. If, in addition, its magnetic moment is due partly to orbital, and partly to spin moment, then we might expect to get results differing from those of ferromagnetic substances in which only spin moment is effective. The most suitable substance was found to be dysprosium oxide (Dy_2O_3) which could be obtained* with 99·9 per cent. purity. Its mass susceptibility is 238×10^{-6} at 15° C.

Description of Apparatus.

Various methods of mounting the paramagnetic substance so as to give minimum moment of inertia for a given magnetic moment were attempted, and finally the following method was evolved. A glass tube of 0·5 to 0·6 mm. diameter and 0·020 to 0·025 mm. thickness of wall was drawn out, and the positions which were as nearly as possible circular in section were selected and straightened by heating under a tension of about 100 grams in a furnace at about 550° C. The glass tube so obtained weighed about 1 milligram per centimetre length. A length of about 8 cms. was sealed off at one end in a small gas flame, and filled with the dysprosium oxide (which was fortunately in a state of fine subdivision). The open end of the tube was dipped in the oxide and the powder which had entered the neck rammed tightly to the bottom with a thin glass rod of slightly less size than the inside diameter of the tube. By successive additions of small quantities of oxide, a length of 6 cm. was filled. The tube was then weighed again to give the weight of powder and broken off to a length of about 6·8 cm. A small piece of shellac, C, was introduced (see fig. 1), the glass end sealed off, and the shellac then melted so as to prevent subsequent motion of the powder. In order to mount the rod, loops of glass fibre (about 0·03 mm. diameter) were prepared by hanging the piece of fibre, weighted at each end, over a thin platinum wire, and passing a current sufficient to allow the glass to soften at the point of contact with the wire. Glass hooks were prepared in a similar manner. A mirror, D, 0·7 mm. × 2·5 mm. in area, is fixed end-on to the lower end of the specimen, this position being chosen to keep the additional moment of inertia low and prevent unnecessary asymmetry. The quartz fibre chosen is attached to the hook at E and shellac melted in the link B whilst the system hangs under its own weight. In the case of specimen 1 (see table below) the " useful " moment of inertia, *i.e.*, that due to the paramagnetic substance, was about 60 per cent. of the total for an external diameter of 0·47 mm. For maximum sensitivity the period of oscillation should be large and usually a period of about 2 seconds was chosen for the specimen, the practicable limits imposed being 1·8 and 3·0 seconds.

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* A. Hilger, Rochester Place, London.

The maximum resonance amplitude reached varies inversely as the logarithmic decrement of the oscillation of the specimen. In air at atmospheric pressure, such a system is practically deadbeat, and in order to obtain only slightly damped oscillations the air around the system must be at a pressure of about 10^{-4} mm. of mercury. For this purpose the torsion head carrying the specimen was of ground glass fitting into the vacuum tight tube T (see fig. 2). The quartz fibre was hung from the lower end of a glass rod which fitted loosely in a glass tube sealed into the torsion head. Wax was melted in at G when the specimen had been adjusted to the correct position. A lens of the $\frac{1}{2}$-metre focus was cemented to the side of the tube opposite the position of the mirror.

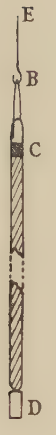


Fig. 1.

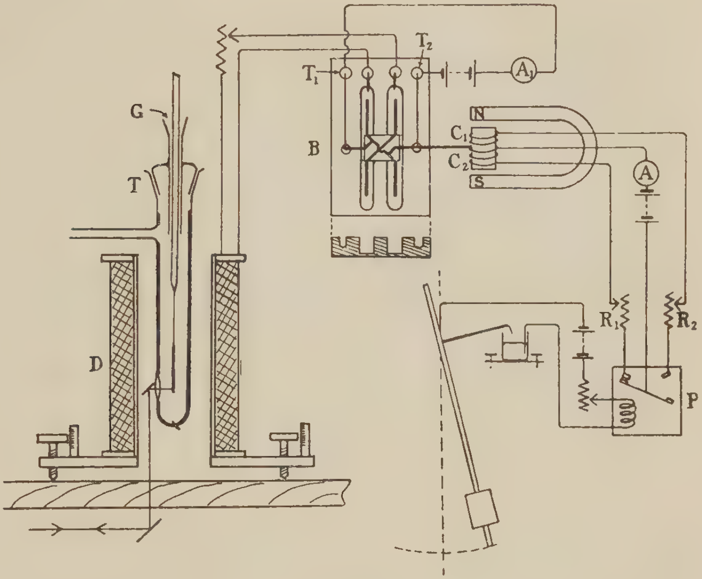


Fig. 2.

As will be seen below, the majority of the disturbing effects depend upon the square of the magnetising field, so that a compromise has to be effected between the conflicting requirements of sensitivity and a minimum of errors. The most suitable value was found to be about 600 gauss so that the magnetising coil was wound to give fields of this value without undue heating. The former for the coil was "paxolin," the tube being 9 cm. internal diameter and 22 cm. long. It was wound with 10 layers of No. 12 S.W.G. D.C.C. copper wire, giving a maximum field at the centre of 35·2 gauss per ampere, with a field of 34·5 gauss per ampere at a distance of 3 cm. from the centre along the axis; the mean field along the middle 6 cm. occupied by the specimen was 35·0 gauss.

The construction of a suitable apparatus for giving alternating current up to 15 amperes, such that the frequency of oscillation of the current could be kept constant to within 1 part in 10,000 presented some difficulty. Any form of alternator appears out of the question and one is faced with the necessity of designing a suitable switch gear, with maintenance apparatus for reversing periodically a direct current of the above magnitude. Furthermore, the frequency must be adjustable to exactly that of the system. After some trials the following arrangement proved satisfactory. The seconds pendulum from an ordinary clock was removed, and another substituted which carried adjustable bobs. One of these could be placed above the centre of oscillation so as to allow of long periods. These bobs allowed the frequency to be continuously variable between the limits required. The burnished pendulum rod is illuminated, and its image projected on to the same scale as that used for the specimen itself. In this way the two frequencies are easily synchronised. A light bar is attached horizontally to the pendulum, at the end of which is a thin copper wire which dips into a mercury cup just as the pendulum passes through the equilibrium position. The mercury of the switch is covered with paraffin, which to a large extent eliminates the erratic action resulting from oxidation of the mercury. This contact closes a circuit carrying about 0·02 amperes through the primary of a polarised relay P (see fig. 2).

The secondary current of the relay is used in the following manner to control the mechanism which operates the mercury reversing switch B for the magnetising current. The two contacts on the output side of the relay go through rheostats R_1, R_2 to the two ends of a coil C_1, C_2, of 400 turns, wound on a soft iron core, which can rotate about a horizontal axis in the field of a large permanent magnet. The centre tapping on this coil passes through an ammeter to a battery of cells and hence to the centre point of the relay. Thus as the pendulum makes or breaks the relay, the current through the tapped coil is reversed. Its rotation is therefore reversed, and by connecting it axially to the mercury switch B, the current in the coil D used to magnetise the specimen is also reversed.

Certain difficulties arise in the design of the mercury switch. Owing to the large inductive arc at break (about 1 cm. in air), the mercury in any ordinary mercury reversing switch soon fouls, with the result that the time interval between " break " and " make " is very changeable. In addition, the switch must be capable of several hours' continuous run without any attention. Vacuum mercury switches were tried, but these were found to be far more erratic in this time interval than the ordinary pattern, in spite of the absence of oxidation. Finally the following device was adopted. Instead of having one pair of mercury pools cross-connected for the reversal of the current, two long channels $9 \times 1 \times \frac{3}{4}$ inch in depth were substituted, whilst the rocker had its wires cross-connected. (The permanent mercury connections from the rocker to the terminals T_1 and T_2 were of course, quite small.) The whole switch was then placed in a bath containing paraffin oil so that all the sparking took place beneath the paraffin surface. The switch would then run from 20 to 30 hours with very little attention, and gave very consistent results.

The time interval between "break" and "make" could be regulated by the rheostats R_1, R_2. Two methods were available for ensuring that this interval was the same irrespective of the direction of the switch. Either the rheostats R_1, R_2 can be adjusted, or, for reasons which appear below, it is better to keep the two currents the same and adjust the levelling screws which support the coil C_1 C_2. To judge this time interval it was found most convenient to use for A_1 a direct current ammeter of quick response, and note the distance through which the needle fell back towards its zero between one "break" and the next "make." Oscillograph measurements showed that this method was very sensitive, a "drop" of 0·4 ampere from 15 amperes representing a time of 0·02 second from the time of maximum current in the one direction to maximum current in the other, whilst a "drop" of 2·0 amperes indicates a time of 0·04 second. As the adjustments could be made to within 0·2 ampere, this means that the time interval could be adjusted to within 0·002 second.

Elimination of Errors.

When an alternating current is passed through the magnetising solenoid, various disturbing couples other than that due to the gyromagnetic effect are produced, and on the satisfactory elimination of these, depends the success of the experiment. The errors may be classed as follows: (*a*) electrostatic, (*b*) mechanical, (*c*) electromagnetic, (*d*) ferromagnetic impurity, (*e*) temperature variation.

(*a*) *Electrostatic Disturbing Effects.*—The sealed glass tube, with its quartz suspension, is a well insulated system, and any electrostatic charge on the specimen will be acted upon by the alternating electrostatic field due to the magnetising coil. Unless precautions are taken this may be of large magnitude, and furthermore, extremely variable. To eliminate this, metallic sputtering of the specimen and suspension was tried, but the difficulty of getting a continuous conducting layer over shellac joints, coupled with the likelihood of ferromagnetic contamination during the process (a point elaborated below) makes the method untenable. Satisfactory screening was accomplished in the following way: the inner surface of the containing tube was platinised and earthed through a platinum wire sealed in at the bottom (see fig. 2). In addition to this, the inner, upper and lower surfaces of the magnetising coil former were covered with tin foil, and both screens earthed. A test of the absence of any error from this source was made by using the mercury switch to apply a large alternating electrostatic potential to the coil. The resultant field produced at the specimen by the magnetising coil was about ten times that in actual experiments, but no movement of the specimen was observed. Should any residual effect be present during measurements, it is easy to show that it is 90° out of phase with the gyromagnetic effect, and will be eliminated along with other disturbing effects which have a similar phase.

It is assumed provisionally that the magnetising field is sinusoidal. It is shown below that only the fundamental of the magnetising current is effective in producing the gyromagnetic angular momentum.

(*b*) *Mechanical Disturbing Effects.*—Non-periodic mechanical impulses may arise due to extraneous causes, and may be troublesome owing to the small damping of the suspended system. The specimen tube was mounted on a slate table built on an " island " floor in a basement room, all remaining apparatus and the observer being clear of this floor. In spite of these conditions it was found that readings could only be taken during the night when outside disturbances were reduced to a minimum.

Periodical mechanical disturbances may be set up owing to the effect of the magnetising coil. No metallic supports could be used for the specimen as the induced currents in them were sufficient to cause rapid oscillations of the specimen. Any direct effect from the magnetising coil was eliminated by mounting it on stout horizontal beams which spanned the " island." Tests were made by using a diamagnetic glass rod instead of a paramagnetic specimen, and alternating a strong magnetising field. Any residual effect will probably have twice the frequency of the magnetising current and hence will only be evident by forcing oscillations on the suspended system, or by a steady displacement of the zero.

(*c*) *Electromagnetic Disturbing Effects.*—The chief disturbances are of the electromagnetic type. In the first instance, the horizontal component of the earth's magnetic field acts upon the changing horizontal component of the specimen's magnetisation and produces a couple of 90° out of phase with the gyromagnetic amplitude. Consequently this can only produce an apparent increase in the magnitude of the latter, and so, by neutralising this effect until the resonance amplitude is a minimum, the error may be eliminated. To reduce its magnitude (which may be hundreds of times that of the gyromagnetic effect) the horizontal moment of the specimen must be as small as possible. The technique of the mounting (see above) keeps the effect small, but even if the geometric axis of the specimen coincides with the axis of rotation, this direction, due to unavoidable asymmetry, may not be parallel with the magnetic axis. A system of trial and error was adopted and proved sufficiently successful, provided that the geometric asymmetry was not too great. The horizontal field of the earth was reduced by two large rectangular coils 4 feet × 3 feet placed with their axes parallel to the meridian. Rotation of the coils about their own axes served to eliminate the residual E–W component of the earth's field.

The horizontal component of the magnetising current may act upon the induced horizontal component of the magnetisation of the specimen, and produce an effect which may be resolved into two components, a couple of twice the frequency of the gyromagnetic effect together with a steady displacement of the zero. This error is minimised, first, by the procedure mentioned in the previous paragraph, and, secondly, by adjusting the coil so that its magnetic axis is parallel to the gyromagnetic axis of the specimen. In general, without any adjustment of the coil, a displacement of the zero sometimes as great as 1 cm. of the scale may be observed when a steady field of about 500 gauss is put on. The adjustment of *one* levelling screw of the magnetising coil D (see fig. 2) brings the spot back to the original zero, in which case we know that the magnetic axis of the specimen and the axis of the magnetising field are in a plane passing through the axis of rotation of the system. There is then no rotational couple; but if the specimen is allowed to oscillate under a steady field, there will be a change of period owing to the fact that the controlling couple is no longer the torsion constant of the suspension c, but $c \pm \mathrm{MH}$, where H is the horizontal component of the field and M the horizontal component of the moment of the specimen. In addition, the reversing of the field causes oscillations of the specimen, due to a couple producing rotation about a horizontal axis, the superposition of these pendulum oscillations on the torsional ones making exact measurements impossible. In the majority of cases MH is positive and would always be so if the directions of field and resulting magnetisation coincide, but owing to the shape of the specimen this is not necessarily so. In either case various positions of the coil (2 levelling screws only being used) are taken in which one screw is raised by constant increments, and the other levelling screw adjusted each time to bring the spot back to the undeflected position. At these positions the period is compared with that of the pendulum, which previously had been synchronised with the free period of the system. The difference is usually small, but by taking a series of positions the correct inclination can be interpolated with sufficient accuracy.

In addition, a disturbing effect of the same frequency as the gyromagnetic effect may arise owing to any asymmetry in the magnetising current acting upon the variable pole of the specimen. To ensure the symmetry of the magnetising current, a water voltameter was placed in the alternating circuit. Equal volumes of gas collected in each limb showed that if the pendulum just closed the relay circuit when in the equilibrium position, the alternating current was sufficiently symmetrical. Any residual component is in phase with the action of the earth's horizontal field on the alternating magnetism of the specimen, and will be eliminated along with that error ; in any case, small differences in the level of the mercury contact in the primary relay circuit caused no apparent difference in either the resonance amplitude or the necessary earth neutralising current.

Other electromagnetic disturbing couples may arise from the switch maintaining gear. Both the primary and secondary relay currents may produce an effect due to the interaction of their horizontal fields with the permanent magnetic moment of the specimen. To minimise this, the relay was kept about 5 metres from the specimen and arranged with its fields vertical. To test for any residual effect, a ferromagnetic specimen was magnetised with direct current and the pendulum tuned to resonance with it. No detectable movement of the specimen was observed with increased relay currents. Finally, the controlling rheostats for the magnetising circuit were similarly disposed, and also placed in the alternating part of the circuit, so that any residual effect is eliminated along with the horizontal component of the magnetising field.

(*d*) *Errors due to Ferromagnetic Impurity.*—Should there be any ferromagnetic impurity present which shows hysteresis, a reversal of the magnetising current (the correct earth's field neutralising current being switched on) will cause a difference in deflection. This couple, is of course, in phase with the one mentioned above, and so is 90° out of phase with the gyromagnetic effect. The prevention of any ferromagnetic impurity proved particularly troublesome. A simple calculation shows that less than 10^{-6} gram of iron *may* produce a steady deflection of about 1 mm. of the scale, this being of the order 10^3 times the gyromagnetic amplitude under these conditions. During the earlier stages of the work, disturbances of the above magnitude were always present and were traced to the shellac used and also the mirrors, which had probably been cut with a steel cutter. Non-ferromagnetic shellac was obtained and the mirrors used were prepared by silvering small pieces of cover glass, the glass being cut with agate. Even though this hysteresis effect may not be perceptible with direct current, it will be detected at resonance by the fact that a large amplitude will be produced when the earth's horizontal field is neutralised. To avoid these smaller traces, extreme care is necessary in handling the specimen. Handling any iron during the course of preparation was usually sufficient to render the specimen quite useless, and for this reason the paramagnetic material was contained in a sealed glass tube, so that subsequent contamination could be removed by washing the specimen in acetone. In spite of this, the "life" of a specimen was usually limited to being mounted about half a dozen times. If there is still any residual effect, it may be eliminated along with the effect of the horizontal component of the earth's magnetic field. It is only when this is small and its effect constant during a set of readings that it is possible to obtain satisfactory measurements. If the hysteresis effect, which has to be balanced out in this way, is about 5 to 10 times the magnitude of the gyromagnetic effect, then its variation usually prohibits accurate measurements.

(*e*) *Errors due to Temperate Changes.*—In order to maintain the specimen in resonance with the pendulum, any change of temperature of the suspension must be avoided. The temperature coefficient of torsional rigidity is small, but the suspended system showed variations due to temperature change in excess of this—probably owing to yield or contraction of the shellac joints causing changes of moment of inertia. It was found essential to keep the temperature constant within 0·25° C. in order to ensure constancy of the period. The magnetising coil was originally wound on a brass former with water cooling, but the induced current in the brass set up rapid pendulum oscillations of the specimen, and finally the coil was wound on a non-conducting tube, with a thin walled brass water jacket intervening between coil and specimen tube.

Method.

The experimental errors detailed above constitute all those which can affect the accuracy of measurement, and of them it will be seen that those which have the same frequency as the gyromagnetic effect, and consequently are evident at resonance, are 90° out of phase, and so can never decrease the amplitude to a value less than that due to the gyromagnetic effect alone. Consequently the method devolves into obtaining the minimum amplitude at resonance. In the early stages of the work, the formula in equation (3) was used, and measurements of the resonance amplitude taken with a series of different earth's field neutralising currents, and the minimum amplitude at resonance taken—this being solely due to the gyromagnetic effect. Two changeable sources of error are likely to be present, and these proved difficult to control. These were, first, changes in the frequency of oscillation of the specimen, as sometimes weeks were necessary before the frequency settled down to a constant value even in the absence of temperature changes. Secondly, if any variable ferromagnetic effect is present, the necessary neutralising current is always changing. The first of these errors will tend to reduce, the second to increase, the amplitude. Later it was found that by maintaining the amplitude with the correct phase, the technique of the observations is considerably simplified. The full theory is given below and shows how this is brought about.

The equation of motion of the system is

$$I\ddot{\theta} + \nu\dot{\theta} + c\theta = T,$$

where I = moment of inertia of the specimen, ν = a damping factor proportional to the velocity, c = the torsion constant of the suspension, whilst T = the turning moment, which may be written

$$T = \frac{1}{g}\frac{2m}{e}\frac{dM}{dt}$$

g is a factor equal to 2 for "spin" and 1 for "orbital" electrons, and is identical with the Landé splitting factor; dM/dt is the time rate of change of magnetic moment.

The magnetic moment

$$M = \chi m_0 H,$$

where m_0 = the mass of the substance used, χ = its susceptibility per unit mass, H = magnetising field, *i.e.*,

$$T = \frac{1}{g} \cdot \frac{2m}{e} \cdot \chi m_0 \frac{dH}{dt}.$$

The current-time form of the magnetising current is not sinusoidal and so

$$H = \sum_{n=0}^{n=\infty} H_0 \cos n\omega t.$$

Measurements are only taken at resonance and hence it is easy to show that only the first harmonic is effective and for a perfect square wave this has the magnitude

$$4/\pi\, H_0 \cos \omega t.$$

Hence we may write

$$T = -\frac{1}{g} \cdot \frac{2m}{e} \chi m_0 \frac{4}{\pi} H_0 \omega \sin \omega t.$$

If there are disturbing effects present they will be in phase with the magnetising current, and may be represented by a term $B\cos\omega t$, so that the complete equation of motion becomes

$$I\ddot{\theta} + \nu\dot{\theta} + c\theta = B\cos\omega t - \frac{2m}{e}\cdot\frac{4\chi m_0 H_0\omega}{\pi g}\sin\omega t,$$

or

$$\ddot{\theta} + 2\kappa\dot{\theta} + p^2\theta = f\sin\omega t + d\cos\omega t, \tag{4}$$

where

$$2\kappa = \nu/I, \quad f = -8m\chi m_0 H_0\omega/\pi e g I, \quad p^2 = c/I, \quad d = B/I.$$

The equation can be written

$$\ddot{\theta} + 2\kappa\dot{\theta} + p^2\theta = f\sin(\omega t + \gamma)/\cos\gamma,$$

where

$$\tan\gamma = d/f.$$

The solution of this is

$$\theta = \frac{f\sin\delta}{2\kappa\omega\cos\gamma}\sin(\omega t + \gamma - \delta) + ae^{-\kappa t}\sin(\omega t + \epsilon), \tag{5}$$

where

$$\tan\delta = 2\kappa\omega/(p^2 - \omega^2).$$

The second part of the equation represents the rate of growth of the amplitude, and for the present only the steady conditions, when the free vibration has died away, need be considered.

At perfect resonance in the absence of disturbing errors, $\gamma = 0$ and $\tan\delta = \infty$, *i.e.*,

$$\theta = -f\cos\omega t/2\kappa\omega.$$

If we arrange the phase of the resulting amplitude, when disturbing effects are present, such that the phase of the oscillation is identical with what it would be at perfect resonance and $B = 0$, then

$$\sin(\omega t + \gamma - \delta) = \cos\omega t,$$

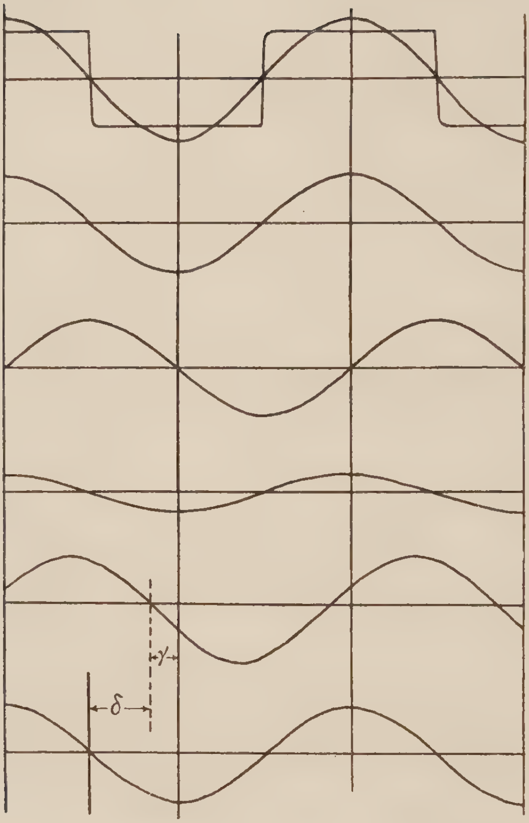
i.e.,

$$\delta = \frac{\pi}{2} - \gamma,$$

therefore

$$\theta = \frac{f\sin(\pi/2 - \gamma)}{2\kappa\omega\cos\gamma}\sin\left(\omega t - \frac{\pi}{2}\right) = -\frac{f}{2\kappa\omega}\cos\omega t.$$

This is identical with the true amplitude provided that the oscillation is in the correct phase, *i.e.*, with the fundamental of the magnetising current. The phases of the various effects are illustrated in fig. 3.



Magnetising Current $\Sigma H_0 \cos n\omega t$ with Fundamental $1 \cdot 27\ H_0 \cos \omega t$.

Galvanometer Oscillation.

Gyromagnetic Effect $= f \sin \omega t$.

Disturbing Effects $= d \cos \omega t$.

Sum of Gyromagnetic and Disturbing Effects $= \dfrac{f}{\cos \gamma} \sin (\omega t + \gamma)$.

Amplitude θ_n/θ_M

$$= \frac{f \sin \delta}{2\kappa\omega \cos \gamma} \sin (\omega t + \gamma - \delta)$$

where $\gamma = \left(\frac{\pi}{2} - \delta\right)$.

Fig. 3.

The double amplitude θ_M is given by

$$\theta_M = f/2\kappa\omega.$$

Making the necessary substitutions we finally get

$$g = \frac{2m}{e} \cdot \frac{2\chi T m_0 H_0}{\pi \lambda I \theta_M}.$$

In order to utilise these conditions, some oscillation having the correct phase must be projected on the scale for comparison with the gyromagnetic amplitude. Oscillograph records showed that the maintaining pendulum is, for a period of 2 seconds, about 16° in advance of this, and this necessitates a correction factor which has a minimum value of 4 per cent. at perfect resonance, but which varies according to the amount of dissonance and involves a knowledge of γ. To obtain a phase exactly that required, a small anchor ring transformer was wound, the primary being in the magnetising circuit and the secondary in series with a bifilar vibration galvanometer, the mirror of which was projected on the same scale as that used by the vibrating system and the pendulum. The original coil of the instrument was replaced by one of suitable moment of inertia to give the correct range of periods required. To investigate the conditions for correct phase, the equations (4) and (5) may be used, putting $B = \gamma = 0$ and also the angle δ, which is here the lag between the fundamental of the induced current and the motion of the coil, equal to 90°. To facilitate this adjustment the coil was air damped so that κ was large. The logarithmic decrement of the coil oscillation was adjusted to be about 0·05, the synchronisation with the pendulum being made with the air damping removed.* Oscillograph records showed that the correct phase was easily obtained. Visual check could be made at any time by comparison with the image of the pendulum on the same scale.

Tests showed that the two amplitudes, that of the galvanometer and that of the suspended system, could be kept in phase to within 10° for a period of 2 seconds. Assuming that the angle δ differs from 90° by this amount we shall get an error of 1·5 per cent., which is below the limit of observation.

Finally, to measure the gyromagnetic effect, the general procedure is as follows: The specimen is hung in position and the direct current tests for ferromagnetic impurity made. These being negative, the system is evacuated to give a logarithmic decrement of about 0·001, and the pendulum synchronised with the specimen. The coil is then adjusted until there is no deflection produced by a direct current, and no change in period under a steady magnetising field. The pressure is then increased to give a logarithmic decrement of about 0·01, the normal working value. The value of the earth neutralising current is so chosen that the phase of the oscillation was the same as that of the galvanometer. A few preliminary trials were necessary to effect this, but once this is obtained, usually no further adjustment of this is necessary during readings.† Under the influence of the alternating magnetising current the amplitude grows as expressed by the term $\theta = \theta_\infty (1 - e^{-2\lambda t/T})$. No readings were taken until the amplitude was about 97 per cent. of the ultimate value, *i.e.*, for $\lambda = 0 \cdot 01$ and $T = 2$ seconds, $t = 6$ minutes, after which the alternating current was continued for 10 to 15 minutes, mean readings of the double amplitude being taken about every half minute. The fluctuations of amplitude were never more than 0·3 mm., whilst in many cases no detectable change was observed.

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* The difference between the undamped and damped periods of the galvanometer for the above conditions causes δ to change by a negligible amount (about 1°).

† If, however, there is any appreciable ferromagnetism, then this current may need adjusting to the extent of 2 or 3 per cent. during the course of a 20 minutes' run. It is usually possible to anticipate this alteration as a change of phase becomes noticeable before any appreciable alteration in the amplitude.

After the measurement of the logarithmic decrement, the moment of inertia of the suspended system is determined by the usual method of measuring the period of oscillation when loaded with a known additional moment of inertia. For this purpose, rings were cut from copper foil 0·008 mm. thick. In view of the smallness of the moment of inertia required, a special design in mounting is necessary. Fine holes pricked diametrically opposite served for the introduction of the ends of an inverted " V " of 50 S.W.G. copper wire for supporting the ring, so that the total inertia is directly calculable. The ring is hung on the hook B (fig. 1) and having a centre of gravity well below the point of support, sets itself under its own weight so that errors due to accidental asymmetry are reduced to a minimum. Two such rings of moments of inertia $4 \cdot 77 \times 10^{-4}$ and $12 \cdot 60 \times 10^{-4}$ were always used, and the calculated values of the inertia of the specimen always agreed within 0·5 per cent.

It only remains to investigate the correction for departure from square wave form of the magnetising current. Oscillograph records were taken and fig. 3 (*a*) shows the shape as traced from a typical record. The deviation from square wave form is small and the time interval between maximum current in the one direction and a similar value in the other varied between 2 and $3\frac{1}{2}$ per cent. of the total, according to the current through the rheostats R_1, R_2, and the depth of mercury in the two elongated pools of the reversing switch. The minimum time represents the inductive lag of the magnetising coil. Taking a value of $3\frac{1}{2}$ per cent. it is easy to calculate the factor of proportionality which should replace the value $4/\pi$ for a perfect square wave. The expansion of H, the magnetising field, as a Fourier series reduces to a single term $H_1 \cos \omega t$, at resonance for a symmetrical magnetising current. For the limiting case quoted above, H_1 is less than $4/\pi$ by about 0·1 per cent., which is, of course, quite negligible.

Table I shows the results for Dy_2O_3 for four different specimens, as indicated by the different masses in column 1. The moments of inertia and time of oscillation of the specimen appear in the second and third columns respectively. The sixth column gives the current which neutralises the horizontal component of the earth's magnetic field and other errors, chief of which is that due to ferromagnetic contamination. In the absence of the latter, 0·104 ampere is

Table I.

Mass $\times 10^3$ grs.	M. of I $\times 10^6$.	T (secs.).	$\chi \times 10^6$.	$\lambda \times 10^3$.	NC$\times 10^3$ amps.	H gauss.	$\theta_M \times 10^3$.	g.
13·5	6·45	2·425	240	9·03	112	446	3·49	1·25
13·5	6·49	2·415	240	11·03	103	285	1·83	1·25
13·5	5·57	2·400	238	11·4	104	518	3·92	1·16
13·5	5·57	2·400	238	14·9	105	455	2·67	1·15
23·4	10·95	2·06	239	8·92	100	474	2·84	1·42
23·4	10·93	2·44	240	9·95	103	494	3·22	1·40
23·4	10·93	2·44	240	9·95	102	308	1·99	1·41
23·4	10·93	2·37	239	11·56	103	322	2·00	1·22
23·4	10·93	2·37	239	11·56	103	504	3·04	1·26
23·4	10·79	2·045	239	11·43	102	512	2·58	1·33
31·4	18·41	2·795	238	11·67	120	315	1·71	1·30
31·4	18·41	2·795	239	11·78	145	515	2·93	1·23
31·4	18·40	2·13	239	8·79	106	517	3·21	1·15
31·4	18·40	2·68	240	12·63	70	446	2·20	1·28
31·6	18·36	1·84	240	7·50	104	494	2·79	1·30

the correct current. If the value differs appreciably from this, ferromagnetism is indicated, which shows itself in the third specimen. The mass susceptibility given is that for the mean temperature during the set of readings, the values being taken from Williams' results.* Each value of θ_M is the mean of a few runs. The scale distance used was usually 60 cm. so that the linear amplitudes range from 2·1 to 4·7 mm. Variations of the moment of inertia of any particular specimen indicate that the specimen had been taken down, and usually cleaned before readjustment, so as to get independent settings. It will be seen that everything possible was varied between practicable limits, so as to eliminate possibility of systematic errors. The values of g considering the smallness of the amplitude are remarkably constant. The mean value is 1·28 with an average departure of 0·07 from this mean.

Discussion of Results.

It remains to compare the results obtained above with other methods of obtaining the factor of proportionality between magnetic moment and angular momentum. As has been indicated above, the value of the constant g indicates that the total moment in Dy_2O_3 is composed of both "spin" and "orbital" contributions. Dysprosium oxide follows the law for normal paramagnetic substances,† *i.e.*, the molecular susceptibility of the substance χ_M varying according to the formula $\chi_M(T - \theta) = C_M$, where T is the absolute temperature and C_M the Curie constant per gram molecule containing 1 gram atom of active substance. From this and from other experimental data we can justifiably assume that the ion Dy^{+++} is the magnetic carrier and that this ion is as free (from the magnetic point of view) as it would be in the gaseous state ; so that if the spectroscopic state of the ion were known it would be possible to calculate its magnetic moment. Unfortunately, the complexity of the rare earth spectra has so far prevented analysis, and the only evidence is from the Heisenberg-Hund scheme,* in which the possible states, determined from the number of electrons, were found by the aid of empirical rules, which the weight of experimental evidence amply justified. Further, Hund† showed that the number of Weiss magnetons,

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* Williams, 'Phys. Rev.,' vol. 12, p. 165 (1918).

† Williams, *loc. cit.*

$$p = 4\cdot97\, g \sqrt{j\,(j+1)},$$

where g is the Landé splitting factor and j the quantum number representing the vector sum of the orbital and spin moments, l and s respectively, and $p = 14\cdot07\sqrt{C_M}$.

He calculated the magnetic susceptibilities of ions of the rare earth group, which with the exception of Eu^{+++} shows close agreement with the experimental values. The theory has been later amplified by Van Vleck,‡ whose formula demands a slight modification in the case of most of the ions in the first half of the rare earth group and completely removes the discrepancy for Eu^{+++} mentioned above. The most probable state of the Dy^{+++} ion is ^6H, the appropriate j value being $(l + s) = 15/2$. The number of Weiss magnetons calculated from this state is 53·0, using the Hund formula, in excellent agreement with the experimental value 51·6 determined from the oxide. This value is supported by susceptibility measurements at room temperature on the octahydrated sulphate§ and on solutions of the sulphate.‖ On the assumption that a Curie law is followed, these results give magneton numbers varying between 52·2 and 53·0.

It is quite possible that the Dy^{+++} ion is not in the lowest state as indicated by the Hund scheme. Neighbouring states as determined by the rules given by Hund (*loc. cit.*) must, of course, satisfy the correct magneton number and the gyromagnetic results obtained above. No such state appears at all probable and one must conclude that the magnetic and angular moments correspond to the ^{6}H state, which gives $g = 4/3$. The experimental results given in this paper point to a value lower than this, although 1·33 is within the limits of experimental error.

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* See Hund, " Linienspectren und periodisches System " (Springer), 1927.

† ' Z. Physik,' vol. 33, p. 855 (1925).

‡ Van Vleck and Frank, ' Phys. Rev.,' vol. 34, p. 1494 (1929).

§ Cabrera, ' J. Physique,' vol. 6, pp. 241 and 273 (1925) ; Meyer, ' Phys. Z.,' vol. 26, p. 51 (1925).

‖ Decker, ' Ann. der Phys.,' vol. 79, p. 324 (1926).

Further work on other paramagnetic substances is in progress, and the results from the iron group should be particularly interesting as, on the one hand, the Hund scheme indicates that varying states should be found with differing g values, whilst the experimental results obtained from susceptibility determinations can only be explained by the arbitrary assumption that throughout the group the ions are in the S state, for which $g = 2$.*

Summary.

A method of measuring the gyromagnetic ratio for paramagnetic substances is described. Hitherto, measurements have been made only on various ferromagnetic materials, all of which show that the source of magnetic moment is entirely due to the spin of the electron. For a paramagnetic substance, the angular moment produced by a change in magnetic moment is very small, and it has been necessary to utilise low frequency resonance for building up the resulting impulse to a measurable magnitude. Errors of measurement are discussed in detail, and shown to be eliminated.

On the assumption that the paramagnetic ion is free, the value of the gyromagnetic ratio involves g, the Landé splitting factor. The method has been employed to determine the value of g for the Dy^{+++} ion in dysprosium oxide. The value $1·28 \pm 0·07$ has been obtained, which indicates that the magnetic moment is composed of both orbital and spin contributions. This is in excellent agreement with the theoretical value 4/3 which corresponds to the $^6H_{15/2}$ state deduced by Hund as being the most probable for this ion.

My thanks are due to the Colston Research Society of the University of Bristol for a grant towards the expenses of the investigation.

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* For a discussion of this point see Stoner, ‘Phil. Mag.,’ vol. 8, p. 250 (1929).

Infra-red Investigations of Molecular Structure. Part V.—The Simplest Kind of Polyatomic Molecule.

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Introduction.

The purpose of the first papers of this series* was the development of a machinery for the determination of the structure of simple polyatomic molecules. Studies of diatomic molecules were the means by which experience was to be gained for the more ambitious work. So much is now known of the diatomic molecule from the analysis of electronic band spectra that most infra-red investigations can only hope to fill in details where, for many examples, the details are already known to a far greater accuracy; and now that confirmation of the essentials of electronic band spectra analysis has been given by the more direct but less precise method of the infra-red and Raman effect,† it is clear that further work upon these lines would be redundant.

The position is far different for even the simplest of polyatomic molecules. It would be unreasonable to expect from the analysis of their band spectra the same degree of theoretical completeness which has been obtained for the diatomic molecule, but there is a necessity that the analyses should at least not conflict with evidence from slightly different but connected spectroscopic fields. Judged by this last criterion, there have been very few satisfactory analyses of the electronic band spectra of polyatomic molecules. On the other hand, as Mecke‡ has urged more than once, there is a real need for the knowledge which the spectroscopy of these molecules alone can give, particularly if physical ideas of molecular structure are to be introduced into chemistry without a long delay. It is this need which is the first justification of the study of the vibration-rotation spectra of polyatomic molecules. At the worst, such work must give data which will make the analysis of electronic band spectra easier and more certain than it is at the moment. For most molecules, as will be seen later, information should follow from the independent analysis of the vibration-rotation bands, apart from the use as a clue to the electronic bands on the one hand, or the mere assignment of a geometrical arrangement to the nuclei on the other.

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* Snow and Taylor, 'Roy. Soc. Proc.,' A, vol. 124, p. 442 (1929); Snow, Rawlins and Rideal, *ibid.*, vol. 124, p. 453 (1929); Snow and Rideal, *ibid.*, vol. 125, p. 426 (1929); Snow and Rideal, *ibid.*, vol. 126, p. 355 (1929).

† Rasetti, 'Phys. Rev.,' vol. 34, p. 367 (1929).

‡ 'Fortschr. Chem. Phys.,' vol. 20, Heft 3; and "Faraday Conference Discussion on Molecular Spectra and Molecular Structure," p. 777.

As this motive had grown in strength during the preliminary work, a beginning was made at once upon the study of the molecules CO_2, N_2O, CS_2, where there was much evidence to suggest that the geometrical form is the same. There was the advantage that the Raman effect* for all of them was known, and that many of the physical properties where spectral data are of direct interest, such as specific heat and dielectric constant, were not settled beyond the possibility of controversy. Two of the three molecules have electronic band systems† whose analysis has not been attempted. Of the three, CS_2 has too large a moment of inertia to make a favourable case for detailed experiment in the infra-red, and CO_2 is being studied at the University of Michigan.‡ Thus the new experimental work in the paper is confined to N_2O, although there are many reasons for considering almost all the conclusions as general to the type. A comparison of the molecules forms a section of the paper, and it will be seen that the treatment of N_2O fits most of the data for the other molecules.

This paper, considered together with the work of the Michigan school§ and of Robertson and Fox,|| should help to make conscious the idea that it is now experimentally possible to determine the structure, *i.e.*, the relative positions of the nuclei for most simple chemical molecules. An advance in theoretical technique in the treatment of the asymmetrical rotator and in experimental

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* Dickinson, Dillon and Rasetti, ‘Phys. Rev.,’ vol. 34, p. 502 (1929) [CO_2 and N_2O].

† Leifson (‘Astrophys. J.,’ vol. 53, p. 73 (1925)) has observed band systems in the Schumann region for CO_2 and N_2O, although that of N_2O is apparently difficult to resolve into a fine structure. A number of heads of bands for CO_2 have been obtained, and fit excellently into the scheme in p. 313 of this paper.

Fox, Duffendack and Barker, ‘Proc. Nat. Acad. Sci.,’ vol. 13, p. 302 (1927), and Duncan, ‘Phys. Rev.,’ vol. 34, p. 1148 (1929) have observed band systems in the region of 3000 A. by the passage of a low voltage arc discharge in a stream of carbon dioxide, but all the evidence is against this as a spectrum of the normal CO_2 molecule. The authors' suggestion of $CO_2{}^+$ seems very much more probable.

‡ I am indebted to the courtesy of Prof. E. F. Barker for this knowledge and for some unpublished work.

§ For a summary of this, which has included work on C_2H_2, C_2H_4, C_2H_6, alkyl halides, etc., see Barker and Meyer, “Faraday Society Discussion,” p. 912.

|| Robertson and Fox, ‘Roy. Soc. Proc.,’ A, vol. 120, p. 189 (1928).

technique for molecules of high moments of inertia is still desirable,* but the claim is not a wild one. Further, it may help to make definite the principles governing the assignment of vibration frequencies in these molecules, and to show the necessity of using these vibration frequencies, obtained perhaps in co-operation with the Raman effect, in the analysis of electronic band spectra. Finally, the building up of the molecule is considered in the light of the values of the vibration frequencies, and it is suggested that sharply defined values of these frequencies correspond to sharply defined bindings whose different chemical natures can in some cases be represented by different spectroscopic names.

Though the extension of this idea to complicated molecules has not yet been done in practice, it is clear that its acceptance makes it profitable to determine the bands due to vibrating groups within complicated molecules, for, although the dynamical behaviour of the whole system cannot be described, there is likely to be much of the chemical environment of the group to be seen for the looking. A few of the chemical applications of this spectroscopic technique are mentioned in the paper, and there are many more waiting to be made.

Previous Work on the Vibration-Rotation Bands of N_2O.

Before this there have been two important investigations upon the vibration rotation bands of the N_2O molecule. The first, in 1908, was by Warburg and Leithauser,† who plotted roughly bands at $4\cdot49\ \mu$, $4\cdot02\ \mu$, $3\cdot86\ \mu$, $3\cdot54\ \mu$. and $2\cdot79\ \mu$. In 1913 Eva van Bahr‡ included N_2O among the gases worked on in her classical paper which, with Burmeister's in the same year, laid the foundation for the present state of the study of vibration-rotation spectra. She experimented only in the bands at $4\cdot49\ \mu$ and $2\cdot86\ \mu$ (the wave-length given by Warburg and Leithauser is inaccurate), the first of which she resolved into a doublet together with the $4\cdot25\ \mu$ band of CO_2 and the $4\cdot66\ \mu$ band of CO.

Since 1913 there seems to have been no serious attempt at the analysis of the bands.

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* The paper of Mecke and Badger (" Faraday Society Discussion," p. 936, and 'Z. Phys. Chem.,' B, vol. 5, p. 333 (1929)) opens up a method of an experimental refinement which the infra-red has never known before, but is unfortunately only applicable to molecules which have at least one fundamental frequency greater than 2500 cm.$^{-1}$. Nevertheless, its use will solve problems which could not possibly have been considered before the innovation.

† 'Ber. D. Chem. Ges.,' vol. 1, p. 148 (1908).

‡ 'Verh. D. Phys. Ges.,' vol. 15, p. 710 (1913).

Experimental.

The spectrometer used was that described in Parts I and III of this series, and the observations were made in the manner described in full in Parts I and II. Since the wave-number interval of the fine structure was always on the lower limit of resolution, the slit width was reduced to a minimum throughout the work; the mechanical width varies from 0·2 mm. at 4·49 μ to less than 0·1 mm. at 2·8 μ. Each of the bands was plotted at least twice, and much of the finer detail has been repeated several times where there seemed a doubt of the irregularities observed. As the bands vary very greatly in relative intensity, the optimum conditions for the analysis of them were different; in fig. 1, which shows the complete band system, the bands are shown at the same pressure of gas, and accordingly their relative intensities may be seen. The correctness of the assignment of the bands to suitable vibrations depends upon the relative intensity as one of the most reliable of guides if the experimental accuracy can be trusted. Measurements of intensity of two different bands were therefore taken under the same conditions on the same night, and the complete diagram of all the bands is drawn from these results.

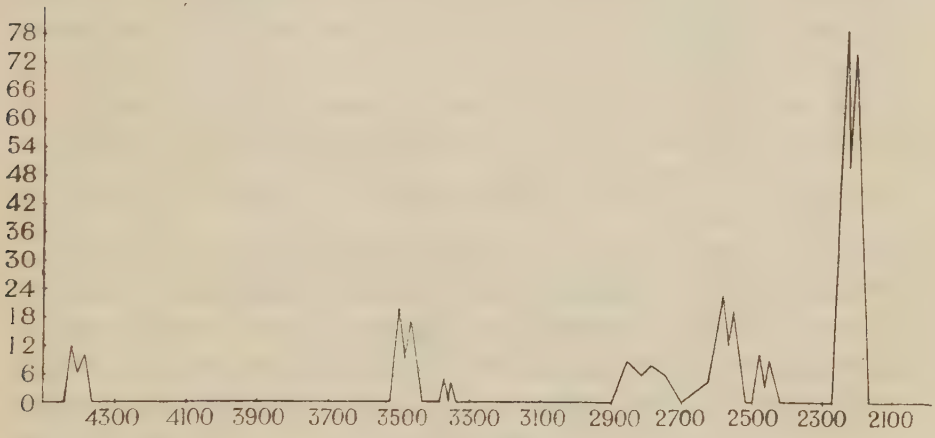


FIG. 1.

The spectra of all the probable impurities in the gas are well known, and accordingly the N_2O was taken from a commercial (dentist's) cylinder.

Results.

In this section the experimental results are given in their entirety, and are separated completely from the inferences which are drawn from them.

Between 2 μ and 7 μ there are seven vibration bands of N_2O, the positions of the centres of which are, in wave-numbers, 2223 (band A), 2569 (band B), 2466 (band C), 2800 (band D), 3487 (band E), 3361 (band F), and 4404 (band G). Above 7 μ the present instrument cannot easily be used, but a search with a prism instrument up to 15 μ has not discovered any more strong bands. The above seven bands are therefore taken as the only vibration-rotation bands of N_2O which are accessible to measurement, unless thick layers of the gas are used. Fig. 1 represents the complete band system.

The centres of the bands cannot be found to an accuracy of more than 1 cm.$^{-1}$, owing to the small separations.

Band A.—The band of the lowest frequency is much the strongest band of the system, and is of the same order of intensity as the 4·25 μ band of CO_2. At 0·5 cm. pressure 30 cm. of the gas absorb 71 per cent. at the maximum at 2238 cm.$^{-1}$. The band consists of a doublet with maxima at 2209 cm.$^{-1}$ (4·53 μ) and 2238 (4·48 μ). [Eva van Bahr's values were 4·49 μ and 4·54 μ.] The classical value for the moment of inertia from this separation of 29 cm.$^{-1}$ is given by $I = \dfrac{RT}{4\pi^2 \nu_r^2 N} = 54 \times 10^{-40}$ gm. cm.^{2}, $\nu_r = 14{\cdot}5$, $T = 293°$.

At 1·5 cm. pressure there is a perceptible fine structure in the region of comparatively small absorption from 2182 cm.$^{-1}$ to 2150 cm.$^{-1}$. This fine structure can be followed through most of the band, except around the maxima, between 0·5 and 1·0 cm., although the interval is so small that it is near the limit of resolution by the instrument. There are well-marked bands, as shown in the table below, separated by approximately 2 cm.$^{-1}$. Whether this is the ultimate fine structure, or whether between these bands are other bands are questions that cannot be completely answered without higher dispersion. Fig. 2 shows the resolution which has been achieved in band A, and in the table below are given wave-numbers corresponding to the heads of the bands of the fine structure.

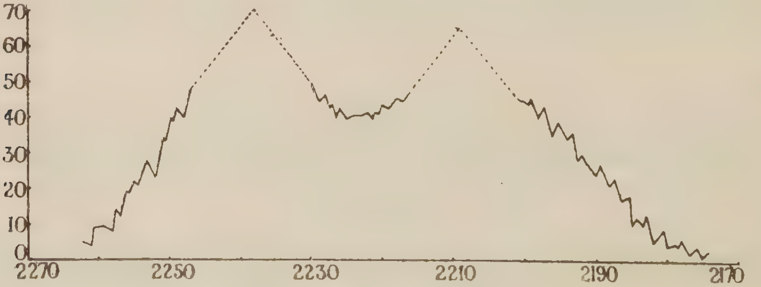


Fig. 2.

R branch (ν ←—).	P branch (ν ←—).
2262·39	2221·97
2260·86	2221·00*
2259·32	2220·04
2257·79	2218·07
2256·26*	2216·08
2255·74*	From 2215 to 2202 unresolved
2253·21	2200·14
2251·19	2199·17*
2250·17*	2197·20
2249·18	2195·24
2247·14	2193·27
From 2246 to 2231 unresolved	2192·30
2230·03	2191·33
2228·03	2189·37
2227·03*	2187·40
2226·01	2185·43
	2184·44*
	2183·15
	2180·78
	2179·40*
	2178·43
	2176·08
	2174·67

Bands marked * are indistinct or weak.

There is a slight convergence of the bands towards higher wave-numbers, in the way which has been observed before in diatomic molecules.

The frequency difference of the more pronounced bands has an average value of 2 cm.$^{-1}$, which is the value of the separation for a rotator of moment of inertia $27 \cdot 5 \times 10^{-40}$ gm. cm.^{2}. This is almost exactly half the moment of inertia calculated from the separation of the doublet.

Band B.—The band with its centre at 2569 cm.$^{-1}$ is much weaker than A, as is shown in fig. 1. Otherwise it differs little from it; it forms a well-marked doublet of separation $27 \cdot 5$ cm.$^{-1}$, has a fine structure of an identical kind,

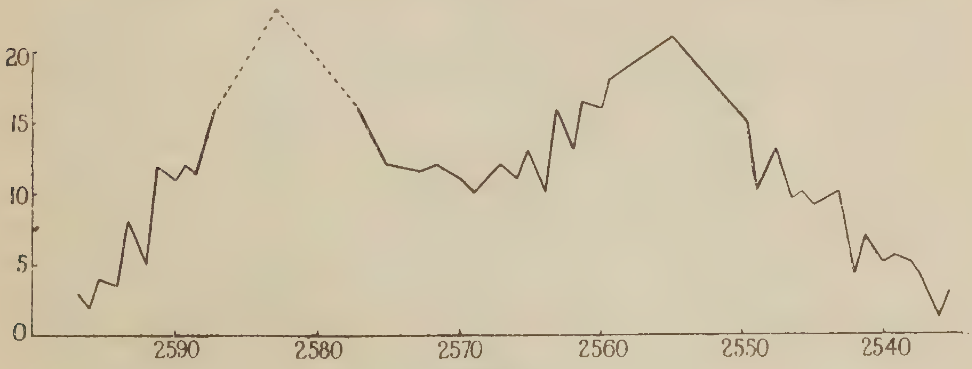


Fig. 3.

though not so well marked, and shows convergence towards higher wave-numbers. The decrease in sharpness of the fine structure may be due to the small resolution at 2500 cm.$^{-1}$. The form of the band is given in fig. 3, and the detail in the table below.

Heads of bands—R branch. [Beyond 2598 the bands cannot be resolved.]	Heads of bands—P branch.
2596·78	2567·27*
2595·38*	2565·30
2593·35	2563·32
2591·34*	2561·44*
2589·36*	2559·51
2587·32	From 2559 to 2551 unresolved
From 2587 to 2579 unresolved	2549·75
	2547·77
2577·33	2545·79*
2575·32*	2543·24*
2571·36*	2541·30
	2539·36*
	2537·40
	2535·36

Bands marked * are indistinct or weak.

Band C.—On the low frequency side of B there is a subsidiary band resembling it in every respect but intensity. The separation of the maxima of the doublet is 27 cm.$^{-1}$, and of such bands of the fine structure as can be obtained the average $\delta\nu$ is c. 2 cm.$^{-1}$, as can be seen from the table :—

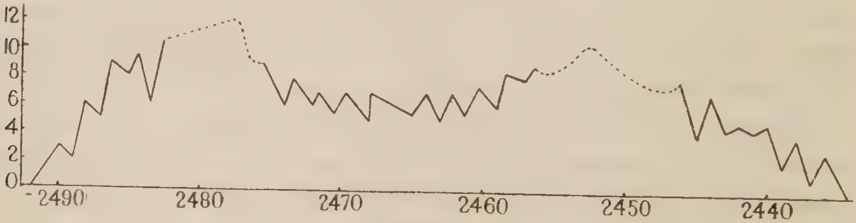


FIG. 4.

R branch.	P branch.
2490·04	2464·00
2488·16*	2462·24
2486·33	2460·33*
2484·40	2458·41*
2482·62	2456·40
2475·25	
2473·41	2446·20
2471·58*	2444·00
2469·72	2442·00*
2467·92	2440·20
	2438·43

Bands marked * are indistinct or weak.

Band D.—The weak band in the neighbourhood of 2800 cm.$^{-1}$ shows a complexity of structure unlike the other bands of the system. No definite resolution was achieved in it, although there is a suspicion of a doublet structure separated by 26 cm.$^{-1}$ with centres at 2800 cm.$^{-1}$ and at 2850 cm.$^{-1}$. The actual form of the band is shown in diagram 1.

Band E.—The band at 3487 cm.$^{-1}$ is of the same order of intensity as B, and has a similar doublet separation of 27·7 cm.$^{-1}$. No success was obtained in resolving its fine structure; this was to be expected at comparatively high frequencies for such small separations.

Band F.—The weakest band detected lies at 3361 cm.$^{-1}$, close to the low frequency side of E. Its doublet separation is 27·3 cm.$^{-1}$.

Band G.—After a long space of transparency between 3600 and 4400 there is one more band with its centre at 4404 cm.$^{-1}$ which is a doublet of separation 26 cm.$^{-1}$.

Relative Intensities of the Bands.

As an aid to the understanding of the results a table of intensities is included, with A, the strongest, as the arbitrary standard of intensity 10. Thus we have :—

A	10
B	1·6
E	1·4
G	0·6
C	0·4
D	0·2
F	0·08

Interpretation.

There are definite criteria which have to be used before the analysis of experimental results of this kind can be anything but an affair of chance. The first of these, and the most certain, is the fine structure of the bands of the system. When this is known with any accuracy, the assignment of the bands should follow at once if the structure revealed fall into one of the well-known categories. (For a clear discussion of these see Barker and Meyer, 'Faraday Society Conference Discussion on Molecular Spectra and Molecular Structure,' p. 912.) The second is intensity, always a critical weapon of the utmost value and often a discriminant between possible assignments where the fine structure analysis is incomplete. Last of the three criteria is the plausibility of the numerical values of the vibration frequencies given to particular intramolecular vibrations. At the end of the present paper considerations are brought forward which, at least for special cases, make it possible to decide upon the source of a given fundamental frequency almost at sight; but, leaving this innovation for the present, we have usually in the values of the vibration frequencies a method of deciding between two assignments. For example, it is improbable in the CO_2 molecule that there could be a fundamental frequency as high as 3600 cm.$^{-1}$, and this might have been used to make the distinction between the linear and triangular forms of the molecule; similarly in any molecule with an XH vibration (with X an element of atomic weight not greater than 20) one fundamental higher than 2000 cm.$^{-1}$ should be expected.

The application of these methods to the band system of N_2O has been carried out in the following way. First, the form and fine structure of all the bands show a close similarity, and the values of I from the doublet separation are the same within the limit of error. There is also the significant fact that the fine structure, though not completely established, appears to give a value of I which is a half of that from the separation of the doublets. These data suggest at once a symmetrical linear molecule o O o, which is the only form where one moment of inertia could be involved ($I_1 = I_2$, and I_3 is very small), and which would be expected to show alternating intensities corresponding to symmetrical and antisymmetrical eigenfunctions of the molecule as a whole with one set of eigenfunctions more probable than the other and hence alternate rotational levels either weak or missing.

The obvious course is to test this hypothesis by attempting to allot the bands of the system upon the basis of a symmetrical molecule. Such a molecule will have two active fundamental frequencies:—

$$\nu_1 \qquad o \leftarrow O \quad o$$

$$\nu_2 \qquad o \quad \overset{\uparrow}{O} \quad o$$

with ν_1 considerably larger than ν_2, and one inactive frequency, which may, however, form active addition bands with ν_1 or ν_2:—

$$\nu_3 \text{ (inactive)} \qquad o \rightarrow O \leftarrow o$$

If the symmetrical molecule is correct, ν_1 is certainly band A (at 2250 cm.$^{-1}$). Its intensity is so great that it must be a fundamental; its vibration frequency is reasonable for what is approximately an N — O vibration, for ω_0 for the NO molecule in its ground state is 1892 cm.$^{-1}$, and we already know that, though the whole molecule is concerned in these vibrations, the effect of the rest of the molecule upon a vibrating group is of the second order when the fields of force are approximately central.

The structure of the band is consistent with this suggestion. If A is ν_1, then for this form of the molecule there is no other high frequency vibration, and B must be regarded as an addition tone of ν_1 and the smaller frequency ν_2. Accordingly, ν_2 must be given a small value of 400–500 cm.$^{-1}$ (there are corrections for anharmony and interaction which are dealt with under the section on molecular constants). The structure of the band fits the simple $\nu_1 + \nu_2$ assignment, and the weak band C may be regarded as :

$$(1-0)\,a_1 + (2-1)\,a_2 + (1-0)\,b_1 + (4-1)\,b_2 + \ldots$$

instead of

$$(1-0)\,a_1 + (1-0)\,a_2 + (1-0)\,b_1 + (1-0)\,b_2 + \ldots$$

where

$$(n'-n'')\,a_1 + (n'-n'')\,a_2 + (n'^2-n''^2)\,b_1 + (n'^2-n''^2)\,b_2 + \ldots$$

is the general form of an addition band. With ν_2 only three times as large as KT, there will be an appreciable number of molecules in the $1\nu_2$ state at normal temperature. Band G, at 4360, may be disposed with as $2\nu_1$.

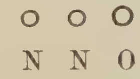
A suggestion which has been made for a similar problem in CO_2* is that the rotation of an approximately linear molecule has to be represented by two quantum numbers, m and i, and that bands involving changes in i occur in pairs corresponding to $\Delta i = \pm 1$. There are objections to this solution for CO_2, although it is valid for many molecules which are symmetrical rotators with two moments of inertia. For the present purpose the difference in intensity between E and F makes its acceptance unsatisfactory. Pairs due to $\Delta i = \pm 1$ are of the same order of intensity.

The confused band D is explained as the superposition of $\nu_1 + 2\nu_2$ and $\nu_2 + 2\nu_3$, the values of which overlap in the region of 2800 cm.$^{-1}$.

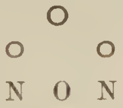
The strong band E, at 3487 cm.$^{-1}$, has too great an intensity to be $\nu_1 + 3\nu_2$, and is best explained as $\nu_1 + \nu_3$, which gives the inactive frequency a value of 1264 cm.$^{-1}$.

The very weak band F may be either $\nu_1 + 3\nu_2$ or $\nu_1 + (2-1)\,\nu_3$ in the way suggested for band C. This is the most unsatisfactory of the assignments, for the first involves arithmetical difficulties and the second intensity difficulties.

The alternative arrangements,



(1)



(2)

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* Colby, 'Bull. Nat. Res. Council,' vol. 57, p. 66 (1926).

each require three frequencies, two of the order of 2000 cm.$^{-1}$ and the other much smaller.

To assume (1), it is necessary to postulate that the structure of A and B is incompletely resolved, and that alternate bands have been missed ; that B and C are one band, the second fundamental ν_2, A being ν_1 as before ; that D is $\nu_1 + \nu_3$, and E $\nu_1 + 2\nu_3$, that is ν_3 is approximately 630 cm.$^{-1}$.

The objections to these assumptions are patent. It is possible but not probable that half the bands have been merged in the limit of resolution ; it is difficult to account for the double doublet structure of B and C (assumed one band) with a vibration along the electric moment of the molecule, and yet the fundamental BC must be ○ → ○ ○ ; the relative intensities of D and E are reversed ; the intensity of the band BC is not of the same order as that of the fundamental ν_1.

The form (2) involves similar difficulties. Either BC or E must be taken as ν_2. If BC, then the objections made above all hold, except that of the form of the band ; the double doublet is a possible form for ν_2 of arrangement (2) ($I_1 = I_2 > I_3$). If E, then the form of the band and its numerical value are difficult to reconcile with its assignment as ν_2. The objection to the relative intensity of the addition bands is removed, but this is the only advantage.

Thus the most natural construction of the form of the molecule from the existing infra-red data is the arrangement of the nuclei symmetrically in a straight line.

Confirmation by the Raman Effect.

The above analysis is strengthened when the Raman effect observations of Dickinson, Dillon and Rasetti are considered. They report that the complete Raman spectrum of N_2O consists of one line, separated from the exciting line by an interval of 1281 cm.$^{-1}$.

This is certainly not an active fundamental frequency. It may be either the inactive frequency of a symmetrical molecule or the difference of two terms having a common third level (*i.e.*, ν_{kl}, where A_{jk}, ν_{jk} and A_{jl} ν_{jl}, the transition probabilities from ν_j to ν_k and ν_j to ν_l, are finite). From the value of the frequencies of bands A and E, 2223 cm.$^{-1}$ and 3487 cm.$^{-1}$, it is clear that the Raman line is numerically equal to the difference between them. Now E may be one of the three bands

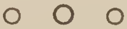
$\nu_1 + \nu_3$ (where ν_3 is the inactive fundamental)
$\nu_1 + 2\nu_3$ (where ν_3 is an active fundamental of frequency c. 600 cm.$^{-1}$)
ν_2 (the second fundamental frequency).

Hence the Raman line may be the inactive frequency of the symmetrical molecule ν_3, or $(\nu_1 + 2\nu_3) - \nu_1$, or $\nu_2 - \nu_1$.

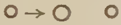
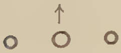
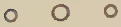
The second of these suggestions is improbable, and it is also not likely that $\nu_2 - \nu_1$ would be the only Raman scattered line. On the other hand, there is much evidence that the inactive frequency is often the strongest Raman line (*cf.*, for instance, Menzies' experiments on powdered crystals). It seems almost certain that is the correct assignment; the meeting of the two lines of evidence is complete and satisfactory.

Molecular Constants of N_2O.

Vibration Frequencies.—We conclude that the molecule of N_2O is a linear symmetrical molecule,



with the three vibration frequencies :—

	Classification in analysis of data.	Value.*
	(A) ν_1	$a_1 + b_1 = 2223$
	ν_2	$a_2 + b_2 =$ c. 400 cm.$^{-1}$
	ν_3 (inactive)	$a_3 + b_3 = 1281$ from Raman effect $= 1264$ from $\nu.r$ spectra and we know that a second order interaction is to be expected.

The a values, or true frequencies without the anharmonic corrections, are referred to in the sub-section on the system of addition bands.

The calculation of a_1 depends upon the recognition of G as $2\nu_1$, *i.e.*, $2a_1 + 4b_1$. Knowing ν_1, *i.e.*, $a_1 + b_1$, we have

$$a_1 = 2244$$
$$b_1 = \quad 21.$$

Another estimate of b_1 may be obtained from the convergence in band A. The proceeding amounts to treating the molecule as analogous to a diatomic vibrator-rotator, subject to similar convergence lines. A is a band due to a symmetrical rotator associated with a vibrator and the lines in it may be described by the transition between energy states of the form:

---

* It should be remembered that a vibration band ν is expressed by $a(n' - n'') + b(n' - n'')^2$, where a is the true vibration frequency, b the constant of anharmony, n' and n'' the quantum numbers of the higher and lower states.

$$E_{nm} = an - bn^2 + B_n m(m+1)\,[1 - u^2 m(m+1)]$$

where $B_n = B_0(1 - \alpha n)$ with $\alpha = 2B(p+q)/a$, p and q being constants characteristic of the potential function, and $u = 2B_n/a$.

m may be assumed to have integral values, and alternate m's will be weak or missing in each state. Allowing for this, that is counting the bands in ν_1 at twice their number, we may substitute bands of known (or approximately known) m and known wave-number into (i), and by taking B_n as 54×10^{-40}, from the separations of envelope and fine structure, arrive at

$$a = 2238,$$

i.e.,

$$b = 15.$$

This is a reasonable value and agrees fairly well with $b = 21$ above. It would also be possible to obtain from the convergence formulæ the constants of the various potential functions which are used to describe the intra-molecular forces. The data upon the fine structure, however, are not sufficiently accurate to make the constants other than misleading. It is hoped that a grating with six times as many lines to the centimetre will enable the overtone to be resolved. With this done, constants of the potential function and the dissociation energy of the NO binding will be given with more justification.

The actual value of ν_1, which is a vibration in a field of force which may be assumed central, is higher than that of ω_0 from the normal $^2\Pi$ NO molecule (1892 cm.$^{-1}$) and has a close resemblance to the ω_0 of the $^2\Sigma$ NO molecule. This is discussed in detail later.

Moment of Inertia.

From the assumption that the rotation bands analysed in ν_1 are separated by 2B, it follows that $B'' =$ c. $0\cdot5$ cm.$^{-1}$. The data which give values for the moment of inertia may then be tabulated:—

Source.	$I + 10^{40}$.
Doublet separation of ν_1 (A)	-54
Fine structure of ν_1 (A)	$(B'' = 0\cdot5)$ 55
Doublet separation of $\nu_1 + \nu_2$ (B)	56
Fine structure of $\nu_1 + \nu_2$ (B)	$(B'' = 0\cdot5)$ 55
Doublet separation of C	57
Doublet separation of D	Possible value of 58
Doublet separation of E	55
Doublet separation of F	56·5
Doublet separation of G	58

The values are quite consistent, and the most reliable figure for I is $54 \cdot 5 \times 10^{-40}$.

This gives a distance between N and O atoms in the molecule of 1·02 Å., and a total length from N to N of 2·04 Å.

The Addition Bands of N_2O.

In the analysis of the band system it was shown that the five bands B, C, D, E, F had to be regarded as combination bands of ν_1 with ν_2 and ν_3. It is now necessary to consider the way in which these are formed in order to obtain an approximation to the true frequencies ν_2 and ν_3.

Born and Brody* have shown, by applying quantum conditions to the classical equations of a vibrator capable of executing vibrations ν_k, ν_l ..., that the energy states of such a vibrator are to be represented by—

$$E_{kl} = h\,\Sigma \nu_k n_k + 1h^2\,\Sigma \nu_{kl} n_k n_l$$

where the second term is of the second order, *cf.* the energy expression

$$E = an + bn^2$$

for an anharmonic diatomic vibrator.

The Born and Brody expression leads to the representation of the band system by

$$\begin{aligned}\nu = {} & (n_1' - n_1'')\,a_1 + (n_2' - n_2'')\,a_2 + (n_3' - n_3'')\,a_3 \ldots \\ & + (n_1'^2 - n_1''^2)\,b_1 + (n_2'^2 - n_2''^2)\,b_2 + (n_3'^2 - n_3''^2)\,b_3 \ldots \\ & + (n_1'n_2' - n_1''n_2'')\,c_1 + (n_1'n_3' - n_1''n_3'')\,c_2 + (n_2'n_3' - n_2''n_3'')\,c_3 \ldots,\end{aligned}$$

where b_1, b_2, b_3, ... c_1, c_2, c_3 are anharmonic constants of the same nature as the $\omega_0 x$ constants for the diatomic molecules, although b_1, b_2 and b_3, c_1, c_2 and c_3 may be either positive or negative, unlike $\omega_0 x$ which is always negative.

From the values of a_1 and b_1 and knowing $a_3 + b_3$ from the Raman effect, we see at once that $(n_1'n_3' - n_1''n_3'')\,c_2$ is -17.

Naturally, we get different values of c_2 itself according to our choice of half or whole numbers for n_1' and n_3'. With whole numbers, $c_2 = -17$; with half, $c_2 = -8 \cdot 5$.

If the weak band F is taken as a $(2 - 1)$ or $(\frac{5}{2} - \frac{1}{2})$ transition of ν_3, it is easy to calculate b_2.

For $3361 = 2223 + 1281 + 3b_3 + 2c_2$ (using whole numbers for n)

$$b_3 = -36 \qquad a_3 = 1317.$$

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* Born and Brody, 'Z. Physik,' vol. 6, p. 140 (1921).

The difficulty of obtaining a third band involving ν_2 makes a similar process for a_2 and b_2 impossible at present. One can estimate a_2 reasonably at 400–500 cm.$^{-1}$. It is convenient to make a complete scheme for the addition bands in which the weak bands C and F fall into the place calculated from the above constants. The scheme is :—

Band.	Assignment.	Wave-number.	n_1''.	n_1'.	n_2''.	n_2'.	n_3''.	n_3'.
B	$\nu_1 + \nu_2$	2569	1	0	1	0	—	—
C	$\nu_1 + \nu_2$	2466	1	0	2	1	—	—
D	probably $\nu_1 + 2\nu_2$ and $\nu_2 + 2\nu_3$	c. 2800	—	—	—	—	—	—
E	$\nu_1 + \nu_3$	3487	1	0	—	—	1	0
F	$\nu_1 + \nu_3$	3361	1	0	—	—	2	1

with the three fundamentals :—

	Assignment.	Wave-number.
A	a_1	2244
Long wave-length	b_1	c. 450
Inactive	c_1	1317

$b_1 = 21$ $b_3 = 36$

The application of this kind of assignment to, say, the spectrum of PH_3 and AsH_3, would remove some of the difficulties in interpretation encountered by Robertson and Fox. The bands in PH_3 and AsH_3 which they call γ, D′ and E″ seem certainly to be due to a (2 — 1) or (3 — 1) transition on the part of the low frequency component of the addition band ; there are other small bands which are probably of a similar origin.

Eucken's analysis of the CO_2 bands upon these lines may be mentioned as one where a complicated series has been unravelled with much success, although there are some details where it would seem desirable to amend it. With more exact data for a_1, b_1, c_1, a_2, b_2, c_2 ... it will become theoretically possible to obtain the constants in the full potential function for a polyatomic molecule :

$$V = \tfrac{1}{2}A_1\phi_1^2 + \tfrac{1}{2}A_2\phi_2^2 + \ldots \tfrac{1}{2}A_3\phi_1\phi_2 \ldots.$$

Rotational Structure of Addition Bands.

The rotational structure of addition bands has not yet been worked out largely because of the lack of any experimental data. In the very simple case of the band B in N_2O we have apparently much the same fine structure as in the fundamentals which, when added together, produce the band; where there is only one moment of inertia, this is a result to be expected, and will almost certainly be found to be true for all the bands of the system when further dispersion can be applied to them. When there are two or three effective moments of inertia the problem is more complicated, but possibly the impetus applied by Mecke and Badger's photographs of addition bands of NH_3 and H_2O will lead to a theoretical attack.

Other Lines of Attack upon the Structure of N_2O.

The account of the molecule given by spectroscopic determination has been drawn to be self-consistent; it is now profitable to consider what is the evidence from other molecular properties.

The electric moment of a symmetrical linear molecule should be zero; for the other possible structures, the electric moment would be finite. The observations of Braunmuhl* gave a value of $0 \cdot 249 \times 10^{-18}$ e.s.u. which is very small. Recent work by Ghosh, Mahanti and Mukherjee† from measurements of the dielectric constant gives a zero value, and provides a strong argument for the structure reached by the present research.

The evidence from measurements of specific heat is not so definite. For the symmetrical molecule o O o we have the usual C_r contribution approaching to 5, together with a Planck term of double weight for the low frequency fundamental, and the ordinary Planck terms for ν_1 and ν_3.

Thus

$$C_v = C_r + 2P\left(\frac{\nu_2}{T}\right) + P\left(\frac{\nu_1}{T}\right) + P\left(\frac{\nu_3}{T}\right)\left[P = \left(\frac{h\nu}{KT}\right) \frac{e^{h\nu/KT}}{(e^{h\nu/KT}-1)^2}\right].$$

At ordinary temperatures the two last terms can be neglected. The uncertainty of the value of ν_2 makes it impossible to give a definite theoretical value to C_v, but from the work in this paper it must lie between $7 \cdot 1$ and $7 \cdot 8$ calories per degree.

For the linear unsymmetrical model O o O the theoretical expression is of the same form:

$$C_v = C_r + 2P(\nu_2/T) + P(\nu_1/T) + P(\nu_3/T).$$

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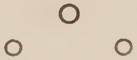
* 'Phys. Z.,' vol. 28, p. 141 (1927).

† 'Z. Physik,' vol. 58, p. 200 (1929).

The analysis showed, however, that ν_2 must be of the order of 650 cm.$^{-1}$. Hence for this form C_ν lies between 6·5 and 6·9 calories per degree.

For the third possibility



the contribution C_v tends towards 6, and the expression is

$$C_v = C_\nu + P(\nu_2/T) + P(\nu_1/T) + P(\nu_3/T),$$

ν_2 is the same frequency as for the first system, and C_v may be between 6·9 and 7·5 calories per degree.

The two most recent experimental determinations of the specific heat* are ·

(*a*) Partington and Shilling. Velocity of sound method $C_v = 6{\cdot}76$.

(*b*) Scheele and Heuse.—Flow method .... $C_v = 7{\cdot}2$.

The discrepancy is great, as is often the case with measurements of specific heat. Measurements made upon CO_2 by Mr. P. S. H. Henry, using the new flow method, indicate that the velocity of sound method is not trustworthy. The value of Scheele and Heuse does not distinguish between the symmetrical linear and the triangular molecule, but the case against the latter has already been made.

The Linear Symmetrical Triatomic Molecule.

In 1926 and 1927 Eucken and Wulf† brought forward many arguments to prove that the CO_2 molecule was linear and symmetrical. The N_2O molecule, in many ways so similar, falls into the same class, which is the simplest kind of polyatomic molecule. All the evidence suggests that CS_2 has also a symmetrical linear structure. The relevant facts show the resemblance clearly :—

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* See Partington, "The Specific Heat of Gases."

† Eucken, 'Z. Physik,' vol. 37, p. 714 (1926); Wulf, 'Z. Phys. Chem.,' vol. 131, p. 90 (1927).

Fundamental bands, from infra-red spectra.	CO_2.	N_2O.	CS_2.
$O \dashrightarrow O \quad O$ (ν_1)	2250	2243	c. 1470
$O — \overset{\uparrow}{O} — O$ (ν_2)	670	c. 450	c. 200
$O \dashrightarrow O \dashleftarrow O$ (ν_3)	1224	1317	c. 800 (From Coblentz' data)
Addition bands of high intensity from infra-red spectra	$\nu_1 + \nu_3$	$\nu_1 + \nu_2$ $\nu_1 + \nu_3$	$\nu_1 + \nu_3$ $\nu_2 + \nu_3$
Moment of inertia. $I_1 = I_2$. I_3 is very small	50×10^{-40}	$54 \cdot 5 \times 10^{-40}$	
Fine structure of ν_1	Prob. alternating intensities	Prob. alternating intensities	
Structure of ν_2	Classical doublet	Inferred to be classical doublet	
Structure of $\nu_1 + \nu_3$	Double doublet	Classical doublet	
Raman effect	1264 1365 two lines* of comparable intensity	1281	655 800 two lines† of comparable intensity
Electric moment	Zero from dielectric constant	Zero from dielectric constant	Zero from dielectric constant
Specific heat	Indicates linear structure	Most reliable value consistent with linear structure	$C_v = 9 \cdot 3$ is consistent with the frequency scheme suggested

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* Dickinson, Dillon and Rasetti, *loc. cit.*

† Gavesan and Venkateswaran, 'Nature,' vol. 124, p. 57 (1929); see also Ghosh and Mahanti, 'Nature,' vol. 124, p. 92 (1929).

The only serious difficulty of this arrangement is the structure of the $2 \cdot 74\ \mu$ band of CO_2 and the doublet inactive frequency given by the Raman effect for CO_2 and CS_2. The ordinary explanation, during the time when CO_2 was considered a thin triangle

with $I_1 = I_2 \gg I_3$, was to consider the molecule as a symmetrical rotator defined by the energy expression

$$E = \frac{h}{8\pi^2}\left(\frac{i^2}{A} + \frac{m^2 - i^2}{C}\right)$$

where A is the moment of inertia about the axis of figure, C the moment of inertia about an axis normal to the axis of figure, and i and m corresponding quantum numbers. In the well-known way, which has received complete verification from the work of Bennett and Meyer upon the alkyl halides, this leads to the transitions

	Vibration.	Rotation.
Vibration parallel to displacement of electric moment	$\Delta n = 1$	$\begin{cases} \Delta m = 0 & \Delta i = 0 \\ \Delta m = \pm 1 & \Delta i = 0 \end{cases}$ Type I
Vibration perpendicular to displacement of electric moment	$\Delta n = 1$	$\begin{cases} \Delta m = 0 & \Delta i = \pm 1 \\ \Delta m = \pm 1 & \Delta i = \pm 1 \end{cases}$ Type II

The second kind of transition gives pairs of bands of the same *m* structure, and the 2·74 μ band of CO_2 was explained as such a band. [It is formed of two doublets with the 30 cm.$^{-1}$ separation characteristic of the 4·25 μ fundamental, the centres of the doublets being separated by 100 cm.$^{-1}$.]

The difficulty of reconciling this view with the form of the 14·7 μ band, which should have a similar structure, but which is in fact identical with the 4·25 μ band, was not met.

When the band is regarded not as a fundamental, but as an addition band of ν_1 and ν_3, the problem remains. ν_1 is a single band of type I, and it is necessary to look upon ν_3 as a doublet. Confirmation is found from the Raman effect, where there are actually two lines corresponding to the inactive frequency. From this Ghosh and Mahanti (*loc. cit.*) have suggested that ν_3 is of type II; this seems hardly justified, for the vibration must be along the line of the molecule, and again we know that the symmetry of the molecule is such that two vibrations perpendicular to each other (the ν_1 and ν_2 vibrations) give bands of similar form at 4·25 μ and 14·7 μ.

Another difficulty raised if the doublet Raman lines in CO_2 and CS_2 are explained as due to $\Delta i = \pm 1$ is the single Raman line in N_2O and the single doublet structure of the addition band $\nu_1 + \nu_3$ in N_2O. The Δi explanation should apply, of course, equally to the N_2O molecule, and yet there is no sign of two Raman lines of comparable intensity, and no sign of the two doublets of the same intensity at 2·86 μ, which are necessary to establish its truth.

It should be noticed that the spectroscopic evidence is self-consistent. The double Raman lines and the double doublet confirm each other, and the single Raman line and the single doublet. The point has been mentioned here in order to show that complete description of the molecules has not yet been achieved. Eucken's suggestion that one of the two doublets in CO_2 is due to a $(2 - 1)\ \nu_3$ transition of the kind used to explain band C for N_2O is unlikely on account of the intensity of the pair.

The effect of all the evidence is to make it seem certain that in CO_2, N_2O, CS_2 we have three molecules of similar structure (structure in the restricted sense defined above), and that they may be looked upon as the simplest kind of polyatomic molecule. Enough is now known of them to make the analysis of their electronic bands possible upon a surer basis than has existed before for any polyatomic molecule. It is the function of the analysis of electronic bands to give detailed information upon the electronic binding, and this must be awaited; there are, however, suggestions to make upon this problem from the values of the vibration frequencies, and that is the subject of the next section.

An interesting beginning in the application of results from vibration rotation spectra to electronic bands may be seen from a consideration of the experimental work of Leifson (*loc. cit.*), who succeeded in mastering the technique of the Schumann region sufficiently to find discontinuous absorption bands for a number of gases. CO_2 was investigated and a number of band heads found, the strongest of which between 1712 A. and 1610 can be represented by

$$\nu = 59102 + 630\, n - 31n^2.$$

It is more than probable that we can identify the 630 with the ν_2 of CO_2 (670), and that the structure of the band systems is of a very simple kind.

*Vibration Frequencies in Polyatomic Molecules.**

During the analysis of the experimental data, it was mentioned that insufficient attention has been paid to the plausibility of the values of the intramolecular vibration frequencies in polyatomic molecules. The criticism is true of work upon vibration-rotation spectra, but has far more force when directed at assignments from the Raman effect and from electronic bands. Since analysis of electronic bands are helped greatly by a knowledge of ω_0'' (the fundamental frequency for the unexcited state of the molecule), and since from the correct values information upon the structure of the molecule is at once provided, it is desirable to develop here considerations which were crystallised during the work upon N_2O and which have been mentioned in another place.

The first significant fact is the value of the N–O vibration in N_2O. (The whole discussion is limited to vibrations in central fields of force, and cannot at present take account of such vibrations as ν_2 for N_2O. That is, we are dealing with vibrations similar in form to those in diatomic molecules. For such vibrations, and only for such vibrations, there is no serious error in giving the

* See also Snow, 'Phys. Rev.,' vol. 35, p. 564 (1930).

name N–O vibration in the place of a vibration involving the whole molecule. It will be seen, in fact, that this error is negligible.) This value is 2244 cm.$^{-1}$, considerably larger than the normal vibration frequency of an unexcited NO molecule, 1892 cm.$^{-1}$. The effect of the mass of the other atom in the triatomic molecule must, therefore, be negligible; the change from NO to the NO vibration in N_2O is a change in binding. Whether this change can have values varying continuously over hundreds of wave-numbers in different environments in different molecules, or whether it corresponds closely to a discrete change in the binding of the NO molecule, is the next question. Now the value of ω_0 for the first excited state ($^2\Sigma$) of NO is 2345 cm.$^{-1}$, which is very near ν_1 for N_2O when a second order correction for the neighbouring N is introduced. This resemblance is suggestive, and begins to be thought more than casual when a collection is made of the values from infra-red and the Raman effect for the —NO group in a number of chemical compounds. Here the variation in mass effect might be thought to be considerable, but actually the value is approximately 1000 cm.$^{-1}$ in all these cases. This is not the normal frequency of NO or the frequency present in N_2O; but it is very like the frequency of the second excited $^2\Pi$ state of NO (1030 cm.$^{-1}$).

It is equally possible to express the vibration frequencies of the CO group in many compounds by a small number (two or at the most three) of discrete values, each corresponding to a different state of the CO molecule, and having a second order correction of not more than 5 per cent., due chiefly to the mass of the atoms to which it is attached.

	ω		
CO in CO_2	2250	The normal state.	*Cf.* ω_0'' for $^1\Sigma$ CO, 2155.
CO in ketones, etc.	c. 1600	The first excited state	*Cf.* ω_0 for $^3\pi$ or $^5\pi$, $\omega_0'' = 1724$.
CO in conjugated ketones CO $\vert$ CO	c. 1000	The second excited state.	*Cf.* ω_0 for the second excited state of CO (possibly $^5\Sigma$), $\omega_0'' = 1104$.

It is probable that there is not the change of binding from CO to CO_2 that there is from NO to N_2O; it must be remembered that the resemblance between the molecules is mainly to be explained in terms of structure and not in terms of electronic binding.

Examples can be multiplied. An interesting one is the CN group in HCN and $(CN)_2$.

In HCN the CN frequency is c. 1500 cm.

$$[\textit{cf.}\ \Pi^2\ \mathrm{CN} \quad \omega_0 = 1728].$$

In $(CN)_2$ the CN frequency is 2100 [*cf.* $\omega_0'' = 2143$ for $^2\Sigma$ CN].* There is also, of course, the example of the XH linkage in different compounds, when the vibration frequency corresponds with the normal frequency of the XH molecule or to the frequency of an excited state slightly different from it.

E.g., CH in CH_4 and aliphatic compounds

3019	*cf.* ^{2}P CH $\omega_0'' = 2800$
OH in H_2O, $\omega_0'' = 3750$	*cf.* ^{2}P OH $\omega_0'' = 3570$

(The vibration frequencies of the known terms of XH molecules are so like that it is difficult to trace a change, if one occurs, in polyatomic molecules. There does seem, however, a definite difference between the CH in any aliphatic compound and the CH in an aromatic compound which should be explicable on these new lines.)

The applications of this principle are obvious. The use of it in its most general form (viz., that the vibration frequency does not vary indefinitely from compound to compound) will save faulty analyses of vibration rotation of electronic band spectra of polyatomic molecules. In its general form too it will act as a delicate discriminant of chemical binding in cases where chemical argument cannot be trusted, *e.g.*, PCl_5, where the existence of two different frequencies for the PCl bond would be a conclusive proof of the two different bindings which Sugden postulates. In its detailed form, when the task of translating into chemistry such spectroscopic changes as that from NO to N_2O has been mastered, it may begin to put a spectroscopic name to valency.

Summary.

(1) An account of experimental work upon the vibration-rotation spectrum of N_2O is given.

(2) The analysis of the data leads to the symmetrical straight line N O N for the form of the molecule.

(3) This form is shown to be consistent with the Raman spectrum of N_2O, the dielectric constant and with one of the two recent determinations of the specific heat of the gas.

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* This suggests that hydrocyanic acid should be written HNC, containing a ^{3}P (divalent) carbon atom. In $(CN)_2$ the carbon atom is $^5S_1$ as would be expected.

(4) The constants of the molecule are

$$I_0'' = 54 \cdot 5 \times 10^{-40} \text{ gm. cm.}^2$$

(there is only one effective moment of inertia of a linear molecule).

$\circ \rightarrow \bigcirc \quad \circ$ $\quad a_1 = 2244 \qquad b_1 = 21$

$\circ \quad \overset{\uparrow}{\bigcirc} \quad \circ$ $\quad a_2 + b_2$ cannot be evaluated from the present data, but is of the order of 400 cm.$^{-1}$

$\circ \rightarrow \bigcirc \leftarrow \circ$ $\quad a_3 = 1317 \qquad b_3 = 36.$

(5) The vibration bands are arranged into a scheme based upon the three fundamental frequencies.

(6) The molecules N_2O, CO_2, CS_2 are compared, and it is shown that, from a structural point of view, they are the simplest kind of polyatomic molecule.

(7) An attempt is made to connect the values of the vibration frequencies of a diatomic group with the electronic binding of the group ; the diatomic group is shown to have frequencies comparable to those of the corresponding diatomic molecule. The importance of the criteria for the assignment of vibration frequencies in the electronic spectra of polyatomic molecules is stressed.

It is a pleasure to thank Prof. T. M. Lowry, for interest and advice upon the development and application of the work, Sir Robert Robertson for encouragement in many ways, Dr. E. K. Rideal, for a stimulating interest which has been appreciated throughout the research, and the Keddey Fletcher-Warr Studentship Board, whose studentship made the work possible.

[*Note added May* 26, 1930.—It is pleasant in a fast-moving subject to note that since the paper was written, two measurements of the electron moment (Zahn, 'Phys. Rev.,' vol. 35, p. 848, and Schwingel and Williams, *ibid.*, p. 855) have been made and agree with the conclusions reached here. Also the experimental work of Dadieu and Kohlrausch ('Ber. D. Chem. Ges.,' vol. 63, p. 251) upon the Raman effect gives very strong support to the last section.]

The Change in the Area and Catalytic Activity of Metallic Surfaces on Passing from the Solid to the Liquid State.

By F. P. Bowden and E. A. O'Connor.

(Communicated by T. M. Lowry, F.R.S.—Received March 27, 1930.)

[Plate 6.]

Some experiments described in a previous paper* have shown that when a metal is made the cathode in a dilute acid electrolyte, the quantity of electricity passed across the interface, in order to cause a given change in the electrode potential, is determined by the accessible area† of the metal surface, and is, to a first approximation, independent of the chemical nature of the surface. The accessible area in this case would correspond to the surface of the metal which is wetted by the electrolyte or which is accessible to hydrogen ions from solution, *i.e.*, it is the area of the metal-electrolyte interface. By a measurement of this quantity of electricity ΔQ it is possible to compare the accessible areas of different metallic surfaces.

That the quantity ΔQ depends on the physical state of the metal surface and is independent of its chemical nature was shown by a comparison of ΔQ for mercury, for liquid amalgams and for platinised mercury. For the sake of completeness it seemed advisable to verify this for metals of quite different chemical composition, and experiments have been made on a fusible alloy and on molten gallium.

In addition to this it was considered to be of some interest to study the change in the catalytic activity of a metal as the surface atoms pass from the crystalline arrangement of the solid to the disorder of the liquid state. Comparatively little information is available upon the catalytic activity of surfaces of molten metals. Some experiments have been made on the rate at which molten tin catalyses the dehydrogenation of alcohol‡ and the reduction of nitrobenzene,§ but from the work of Gwyn Williams|| it would appear that the catalytic activity is due mainly to traces of oxide on the surface.

A measurement of the rate at which metal cathodes catalyse the evolution

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* Bowden and Rideal, 'Roy. Soc. Proc.,' A, vol. 120, p. 59 (1928).

† Bowden, 'Nature,' vol. 122, p. 647 (1928).

‡ Sabatier and Mailhe, 'Ann. Chim. Phys.,' vol. 20, p. 289 (1920).

§ Brown and Henke, 'Z. Phys. Chem.,' vol. 27, p. 739 (1923), and vol. 28, p. 71 (1924).

|| Williams, 'Trans. Faraday Soc.,' vol. 25, p. 446 (1929).

of hydrogen from dilute acid solution gives a convenient method of studying the activity of the metals for this reaction. In this paper, measurements are described with cathodes of a fusible alloy, of pure gallium and of mercury. By a simultaneous measurement of ΔQ the accessible area of the surface can be calculated. It is found that ΔQ is approximately the same for all three surfaces ; the earlier conclusions are thus confirmed.

It is shown that the total catalytic activity of a metal surface for a particular reaction depends upon three factors which can be measured separately.

(i) *The Accessible Area of the Surface.*

A knowledge of the accessible area of a metallic surface is so important, and there seem to be still so many misconceptions about the methods of determining it, that it is desirable to compare the methods which have been employed. One of the earliest methods developed by Paneth and his co-workers was to measure the quantity of a radioactive salt* or of methylene blue† which was adsorbed by the surface. If it forms a monomolecular layer (there is experimental evidence for this in the adsorption of methylene blue on diamond dust) the area of the surface can be calculated. This method is an ingenious and useful one but it can usually be applied only to powdered substances. It must be used with extreme caution since there is much evidence‡ to show that the material is not always adsorbed in a complete monomolecular layer. In the method which has been developed by Constable§ the metal surface is oxidised and the thickness of the film measured by interference colours. The area of the surface can be estimated if a number of assumptions are made, that the optical properties of the underlying surface are known, that the refractive index and chemical composition of the oxide layer are known, that the layer is homogeneous and that the density is that of the oxide in bulk. Evans and Bannister|| have shown that these assumptions are not justified ; by a direct weighing of the metal specimens, and other methods, they showed that there is no direct relation between the real thickness of the film and the interference colour. As a result of their calibration it is now possible in the case of a silver iodide film to determine the thickness of the film by its colour. Applied to the study of the structure of the *surface region* of a metal, this

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* Paneth and Vorwerk, 'Z. Phys. Chem.,' vol. 101, p. 480 (1922).

† Paneth and Radu, 'Ber. D. Chem. Ges.,' vol. 57, p. 1221 (1924).

‡ Bancroft and Barnett, 'Coll. Symp. Mon.,' vol. 6, p. 73 (1928).

§ 'Roy. Soc. Proc.,' A, vol. 119, p. 196 (1928).

|| 'Roy. Soc. Proc.,' A, vol. 125, p. 370 (1929).

method would be a valuable one, but, since it necessarily involves the destruction of the metal surface to a depth of some thousand atoms, and since it does not detect irregularities of less than 10^{-5} cm. it cannot give information upon the area and configuration of the surface atoms. For an investigation of reactions proceeding on surfaces it is a knowledge of these surface atoms which is of the first importance. The area measured by the electrolyte method is that which is accessible to hydrogen ions from solution; it is thus sensitive to irregularities of molecular dimension in the actual surface of the metal. It has again been suggested* that the method depends upon the assumption that different metals which have the same surface area will require the same quantity of electricity across the interface to produce a given change in the potential. If this were an assumption there is theoretical evidence for it; it is in reality a direct experimental observation.

The accessible area of rolled metal may be twice, and of sand-papered, ca. 6 to 10 times its apparent area. If the surface is activated by alternate oxidation and reduction the area may be increased to ca. 46 times its apparent area. If a metal sponge is formed on the surface by corroding it with acid or by electrodepositing, as in platinum black, the accessible area may be some 800 to 1000 times the apparent area. If the metal has solidified from the liquid state, the accessible area is comparatively small, some 1·5 to 1·7 times its apparent area. It is probable that the surface of the metal solidifies in a smooth condition, but, when this surface layer is removed by polishing with sand-paper or by etching, cracks and irregularities develop, relieving the strains in the surface layers of the metal. Evidence for narrow cracks penetrating deeply below the surface of polished metals has been obtained by Evans.† It is shown that the accessible area is one of the main factors which determine the apparent catalytic activity of a metal surface.

(ii) *The Configuration of the Surface Metal Atoms.*

It is to be expected‡ that the catalytic activity of a metal will be dependent on the particular arrangement of the metal atoms in the surface layer. Atoms which are partially out of the crystal lattice, or which are aggregated only in minute crystals, or which are situated in crystal edges will possess a higher surface energy than the more stable atoms existing in the lattice of a large

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[*] Adam, "The Physics and Chemistry of Surfaces." ('O.U. Press,' 1930), p. 246.

[†] 'J. Chem. Soc.,' vol. 355, p. 2651 (1929).

[‡] See Taylor and Kistiakowsky, 'Z. Phys. Chem.,' vol. 125, p. 341 (1927).

crystal. In general these atoms will contribute more to the catalytic activity of the surface.

Measurements of the rate at which metals catalyse the evolution of hydrogen support this view, but usually the effect of altering the configuration of the metal atoms is small compared with the effect due to a change in the accessible area of the surface. It would appear that the main effect of "activating" a metal surface by oxidation and reduction or by the formation of a metal sponge is to increase the accessible area. Accompanying this there is a smaller variation in the specific catalytic activity (*i.e.*, the activity per unit of accessible area) due to the altered configuration of the surface atoms. Under some conditions this second effect may become quite large. For example the reduction of a monomolecular layer of oxide* causes little change in the accessible area, but produces a marked increase in the catalytic activity. This activity decreases with time, due probably to a sintering of the metal atoms. This diminution in activity with ageing of the surface is quite general for all the metals.

There is a sudden decrease in the specific catalytic activity of a metal as it passes from the solid to the liquid state. Such a decrease is to be expected since the metal atoms are now able to fall into a position of minimum surface energy.

(iii) *The Chemical Nature of the Metal.*

The catalytic activity of a metal should also be dependent upon its chemical nature. It is difficult to arrange the metals in the order of their intrinsic catalytic activity because the activity varies so much with the physical condition of the surface. A comparison of different metals should be made under corresponding surface conditions. This can hardly be realised with solid metals; in fact, it is not easy to prepare two samples of the same metal which will show the same activity, even when the methods of preparation are apparently identical. An approximation to a corresponding surface condition is reached when the metal is liquid, and in this state the surface shows a constant and reproducible activity. In this paper a comparison is made of the catalytic activity of different liquid metal surfaces under corresponding conditions. The activity is dependent to a marked extent upon the chemical nature of the metal; a surface of fusible alloy catalyses the evolution of hydrogen ca. five times, and molten gallium ca. eight hundred times as fast as a mercury surface.

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* 'Roy. Soc. Proc.,' A, vol. 125, p. 446 (1929).

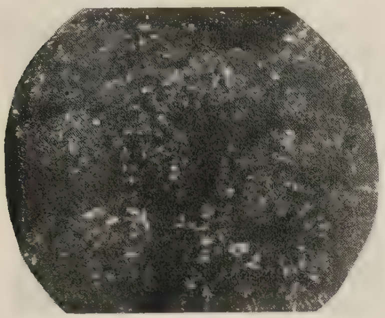

FIG. 1A.—Solidified alloy. (×12.)
Accessible area 1·4.

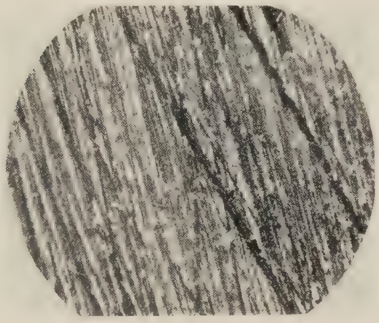

FIG. 1B.—Sand papered alloy. (×12.)
Accessible area 6·3.

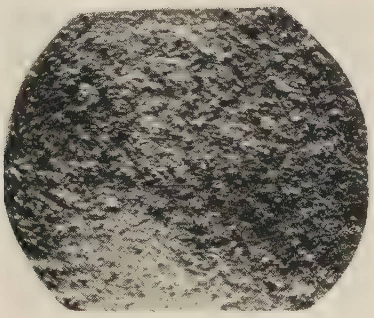

FIG. 1C.—Corroded alloy. (×12.)
Accessible area 800—1000.

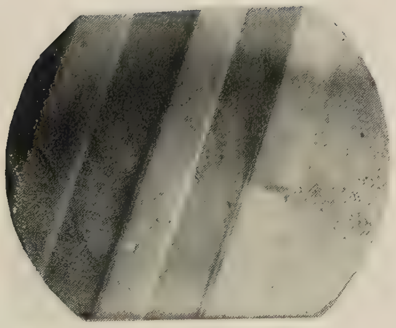

FIG. 5A.—Solidified gallium.
Accessible area 1·7.

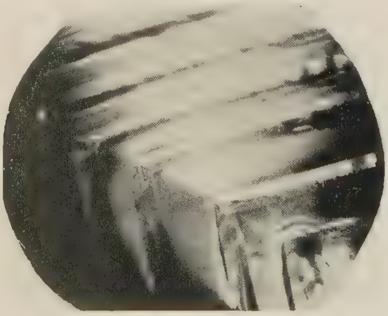

FIG. 5B.—Dendrite in solidified gallium.
Note long crystalline structure.

It has been suggested* that the mechanism by which a metal surface catalyses the evolution of hydrogen from solution is not very different from that by which it catalyses many heterogeneous gas reactions, and the work of several investigators has shown that there is a parallelism between the rates at which these reactions proceed. In the light of this it is apparent that the above conclusions can, with the appropriate precautions, be applied to the case of the catalysis of heterogeneous gas reactions.

FUSIBLE ALLOY.

Experimental.

The electrode vessel was similar to that which has previously been used for a mercury cathode,† and the same method was adopted for filling it with oxygen-free electrolyte. The electrolyte was N/5 sulphuric acid freed from dissolved air by boiling out under reduced pressure and stored under hydrogen. A fusible alloy (melting point 70°) of bismuth, lead, cadmium, and tin, of approximately the same constitution as Wood's metal, was used as the cathode. This was admitted to the cell in the molten condition, and the usual precautions were taken to ensure that the surface was free from oxide. Measurements were made of the quantity of electricity ΔQ which must be passed across the metal/electrolyte interface in order to cause a given change in the electrode potential, and also of the relation between the electrode potential and the current density. From the quantity ΔQ the accessible area of the surface can be evaluated. The current density gives the rate at which hydrogen is being liberated at the surface and is a measure of the catalytic activity of the surface for this reaction.

After measurements had been made on the fusible alloy, it was removed from the cell, replaced by mercury, and the measurements repeated. In this way a direct comparison was made between the two metals.

Area of the Surface.

After ΔQ had been measured with the alloy in the liquid state, it was allowed to solidify and ΔQ again measured. The solid surface was then treated in different ways, by rubbing with glass paper and by etching with acid, and ΔQ measured in each case. The values obtained for the accessible areas of these surfaces are summarised in Table I, the mercury surface being in all cases the unit of comparison.

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* Hammett, 'J. Amer. Chem. Soc.,' vol. 46, p. 7 (1924); Bowden, 'Roy. Soc. Proc.,' A, vol. 126, p. 107 (1929).

† 'Roy. Soc. Proc.,' A, vol. 126, p. 107 (1929).

Table I.

Nature of surface.	Accessible area (compared with mercury).
Liquid alloy	1·0
Solidified from liquid state	1·4
Solid surface rubbed with glass paper	6·3
Solid surface etched with nitric acid until surface covered with a metal sponge	800–1000

These results show that the area of the surface of the liquid alloy is the same as that found for a mercury surface, a result in agreement with the earlier work. This surface appears smooth and bright. Its appearance under the microscope is shown in Plate 6, fig. 1A.* On rubbing the surface with fine glass paper the area increased to 6·3. Under the microscope the surface appeared scratched and torn with many deep grooves (fig. 1B).

Etching the alloy with nitric acid until the surface was covered with dark adherent metal sponge increased the area greatly, 800–1000 times its apparent value. This is shown in fig. 1C. Owing to the low reflecting power of the surface this photograph was taken with indirect illumination. For *a* and *b* vertical illumination was used. When each of these surfaces was fused, the area of the liquid surface returned to its original value of one. These values for the surface area are in good agreement with those found for other metal surfaces in similar circumstances.

Change in Catalytic Activity on Fusion.

In fig. 2 the electrode potential is plotted against the temperature for a cathode of this alloy when hydrogen is being liberated on its surface at a constant current density of 4×10^{-5} amps. cm.^{2}. The potential of the hydrogen electrode in the N/5 sulphuric acid was $-0 \cdot 3$ volt sat. cal., so that the points correspond to a considerable hydrogen over-potential. The left-hand branch of the curve is for the smooth solid alloy and shows the normal decrease in overpotential with temperature. The temperature coefficient was ca. 0·0037 volt per degree. At the point A the alloy began to melt and the overpotential rose rapidly; at the point B fusion was complete, and the overpotential, at the new value on the liquid surface,

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* We are indebted to Mr. F. I. G. Rawlins for taking these microphotographs.

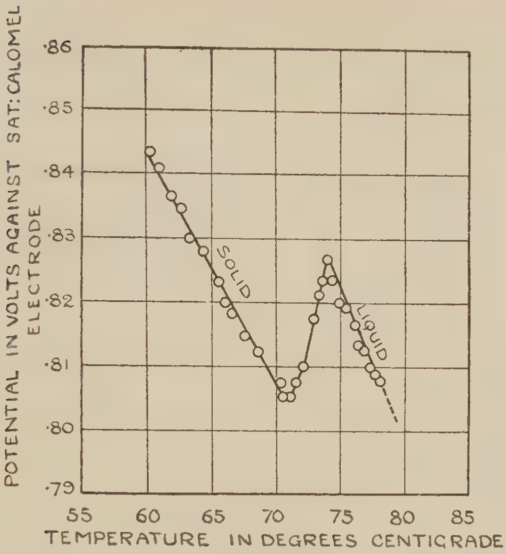

FIG. 2.

again fell regularly as the temperature increased. The change in overpotential on fusion is even more marked for a surface which has been corroded. This is shown in fig. 3.

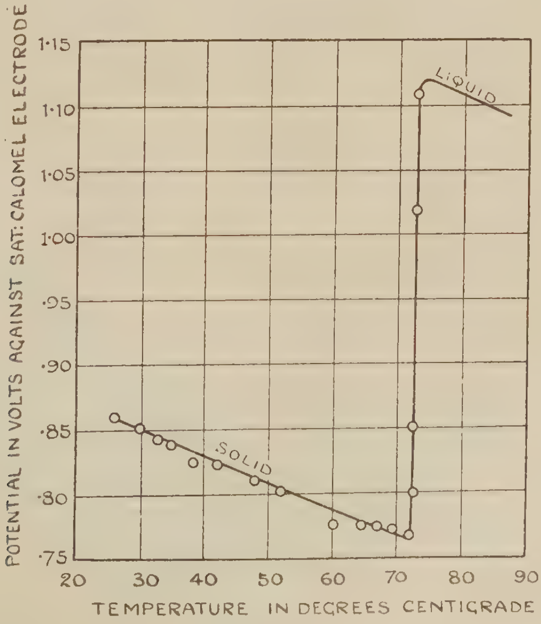

FIG. 3.

This increase in overpotential on fusion means a decrease in the catalytic activity of the surface for hydrogen evolution. The rate of evolution of hydrogen at these surfaces under identical conditions of temperature and potential are given in Table II.

Table II.—Temperature 70° C. Potential —0·893 volt.

Nature of surface.	Rate of hydrogen evolution coulombs per second per apparent square centimetre.
Liquid	5×10^{-5}
Solidified	10×10^{-5}
Etched	6000×10^{-5}

Comparison of Activity for Solid Surfaces.

The effect of different methods of treatment on the rate at which the solid surface catalyses the deposition of hydrogen under identical conditions of temperature (15° C.) and potential (—1·0 volt cat. cal.) is shown in the second column of Table III.

Table III.

Nature of surface.	Rate of deposition of hydrogen per square centimetre of apparent area.	Accessible area.	Rate per square centimetre of accessible area.
	coul. sec.		
Solidified from liquid	13×10^{-6}	1·4	9×10^{-6}
Sand-papered	30×10^{-6}	6·3	5×10^{-6}
Etched with nitric acid	17000×10^{-6}	1000	17×10^{-6}

The velocity per apparent square centimetre on the etched surface is some thousand times greater than that on the smooth surface. The last column of the table shows the reaction velocity per square centimetre of accessible area, which is a measure of the specific catalytic activity of the surface. This is seen to be of the same order for all the surfaces, a result which indicates that the great increase in catalytic activity on etching is due mainly to an increase in the surface area. Accompanying this increase there is a smaller change in the catalytic activity due to an alteration in the structure of the metal surface itself. Although the accessible area is the chief factor in determining the catalytic activity of a particular metal, the configuration of the atoms in the metal surface is responsible for a definite, though smaller, effect.

GALLIUM.

In studying these changes in the catalytic activity which occur on fusion it is an advantage to have an electrode of a pure metal, for in this way alone a surface layer of known and unvarying chemical composition is secured. The only suitable metal for this purpose was pure gallium, which melts at 30° C., and experiments have been carried out on a cathode of this metal.

Preparation of Gallium.

The metallic gallium was prepared from a quantity of slightly impure gallium oxide.* The oxide was heated to 500° C. in a pyrex glass tube and converted into the chloride by the action of carbon tetrachloride vapour. The vapour was introduced by bubbling nitrogen through warm liquid carbon tetrachloride and was passed over the heated oxide in a continuous stream. The easily volatile gallium chloride (boiling point ca. 210° C.) distilled over and condensed in the cooler part of the tube. The chloride was then purified by carefully subliming twice in an apparatus similar to that described by Dennis.† The pure anhydrous chloride so obtained was dissolved in a mixture of hydrochloric acid and ice which had previously been cooled in a freezing mixture. This cooling is necessary to prevent the heat of solution from causing hydrolysis of the chloride and loss by volatilisation. The solution was filtered to separate insoluble carbon compounds, chiefly hexachlorethane, and then neutralised with potassium hydroxide. The precipitated gallium hydroxide was filtered off, washed, and dissolved in slight excess of potassium hydroxide. This solution was electrolysed, using a platinum anode and a short bright platinum wire as cathode. A current of ca. 1 amp. was passed and the cell was kept cool by packing in melting ice. The main product of electrolysis was hydrogen, but liquid metallic gallium separated out and was collected as it dropped from the cathode.

Experimental.

The cell used for the gallium was similar to that described for the fusible alloy, but owing to the relatively small quantity of gallium available the arrangement for admitting the cathode was slightly modified. The cathode container was in this case a small shallow glass cup with a short platinum contact wire sealed into a depression in its centre. This was supported by a glass tube which passed through the stopper in the top of the cell. The cell was filled with warm, oxygen-free electrolyte and the polarising current connected, so that hydrogen was evolved from the platinum contact wire. Since gallium is very readily oxidisable, precautions had to be taken to ensure that the cathode surface was free from oxide film. The liquid gallium was blown by hydrogen pressure through a fine capillary into a reservoir at the top of another long capillary tube of fine bore. This second tube passed through the top of the cell and led to the cathode container. The oxide-free gallium was forced through this tube into the container. In this way the gallium surface was made cathodic during its growth under the electrolyte and was free from oxide or adsorbed oxygen. The metal formed a bright drop, ca. 0·9 cm. long by ca. 0·4 cm. high. There was no appreciable change in shape on solidification.

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* The gallium oxide was generously given us by Prof. C. A. Kraus, of Rhode Island University, to whom our thanks are due.

† Dennis, 'J. Amer. Chem. Soc.,' vol. 48, p. 2026 (1926).

Change in Catalytic Activity on Fusion.

It is found that gallium catalyses the evolution of hydrogen rapidly, so that relatively large current densities are necessary to establish a high hydrogen overpotential. In fig. 4 is shown the change in potential on fusion when the cathode is polarised with a constant current density of 2×10^{-4} amps. cm.^{2} The left-hand branch of the curve is for the solid metal and shows a decrease in the overpotential of 0·0025 volt per degree. At the temperature of 30° C. fusion occurred and the potential rose rapidly some 130 millivolts. When fusion was complete, the overpotential on the liquid metal again decreased with rising temperature, and after a few degrees fell steadily with a slope of 0·0034 volt per degree.

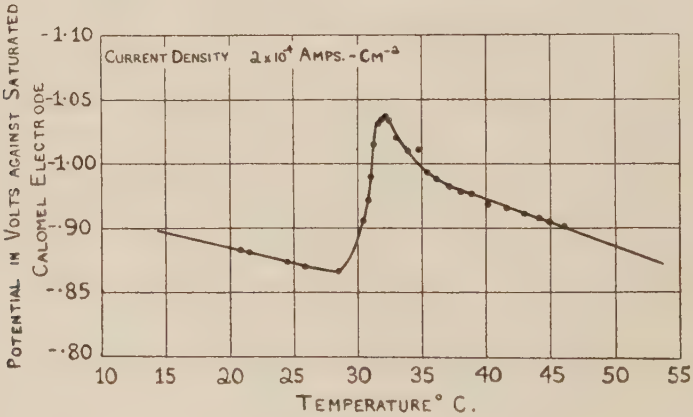

Fig. 4.

After measurements were completed on the gallium it was removed and replaced by an equal volume of mercury and the measurements repeated. The surface area of this mercury drop was approximately the same as that of gallium, so that a direct comparison was made between the two metals. Owing to the greater density of the mercury, the drops were not quite the same shape, but the error introduced by this was small.

Accessible Area of Surface.

The high catalytic activity of gallium for hydrogen deposition makes it difficult to determine the accessible area of the surface with accuracy. In order to establish an appreciable overpotential, high current densities are necessary, and in consequence the potential changes are very rapid. Within the limits of experimental error the accessible area of the liquid gallium was the same as that of mercury, and on solidification the accessible area increased to ca. 1·7 times its apparent area. The nature of this solid gallium surface is shown by the microphotographs (A) and (B), fig. 5 (Plate 6). Most of the surface has a long crystalline structure, as in (A).

Activity of Surface.

A comparison of the activities of the liquid and the solid gallium surfaces under identical conditions of temperature and potential is given in Table IV.

Table IV.—Cathode potential —0·87 volt. Temperature 30° C.

Surface.	Rate of hydrogen evolution per apparent square centimetre.	Rate of hydrogen evolution per square centimetre of accessible surface.
	coulombs second	coulombs second.
Liquid gallium	11×10^{-5}	11×10^{-5}
Solid gallium	28×10^{-5}	17×10^{-5}

The last column gives the rate of hydrogen evolution per square centimetre of accessible surface and is a measure of the specific catalytic activity of the surface. When the gallium atoms are arranged in the crystalline lattice they are more active than when in the liquid state.

Comparison of Activity of Liquid Metals.

It is of some interest to compare the catalytic activities of different metals in the liquid state. The physical conditions at the surface are then identical and any differences which appear in the activities are due to the intrinsic chemical nature of the metal atoms. In fig. 6 the logarithm of the current density is plotted against the potential for cathodes of mercury, liquid alloy and liquid gallium, under identical experimental conditions. It is evident that there is a marked difference in the rate at which these metals catalyse the evolution of hydrogen. A comparison of the rates under identical conditions of temperature and potential is given in Table V.

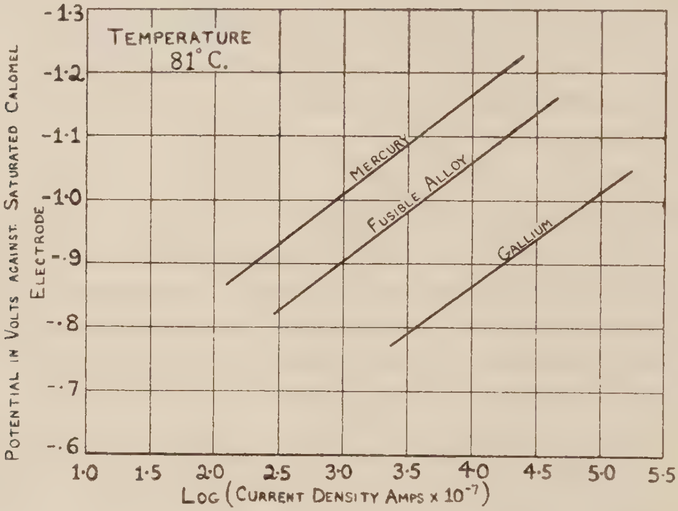

FIG. 6.

Table V.—Potential —0·87 volts. Temperature 81° C.

Surface.	Rate of hydrogen evolution per square centimetre.
	coulombs per second
Mercury	20×10^{-6}
Liquid alloy	100×10^{-6}
Liquid gallium	1590×10^{-6}

The liquid gallium surface catalyses the reaction some 800 times faster than a mercury surface.

Summary.

Measurements of the surface area of electrodes of fusible alloy and of gallium have confirmed the previous work that the accessible area of all liquid metals is sensibly the same.

On solidification the area increases; for solidified alloy ca. 1·4 and for solidified gallium ca. 1·7 times its apparent area. The accessible area of sand-papered alloy is ca. 6·3 and of corroded alloy ca. 800 times its apparent area.

The total catalytic activity of a metal surface for a particular reaction depends upon three factors which can now be separated and the part played by each measured :—

(i) The accessible area of the surface. Usually this is the most important factor. The main effect of "activating" a metal surface by oxidation and reduction, or by the formation of a metal sponge on the surface, by corrosion, or by electrodeposition is to increase the accessible area of the surface.

(ii) The configuration of the surface metal atoms. The alteration in activity due to a change in the arrangement of the surface metal atoms is usually small compared with (i). Under some conditions it can become quite large. There is a sudden decrease in the activity as the surface atoms change from the crystalline to the liquid state.

(iii) The chemical nature of the metal. The activities of different metal surfaces are measured under corresponding physical conditions. The activity of a metal is dependent to a marked degree upon its chemical nature. Fused alloy is ca. five times and fused gallium ca. 800 times as active as mercury.

It is with very much pleasure that we express our thanks to Prof. T. M. Lowry for criticism, Dr. E. K. Rideal for interest and encouragement throughout the progress of the work, and to the Royal Commissioners of the Exhibition of 1851 for the grant of a Senior Studentship to one of us.

Experiments on the Excitation of Light by Low Voltage Positive Rays.

By E. T. S. Appleyard, B.A.

(Communicated by Sir Ernest Rutherford, P.R.S.—Received April 29, 1930.)

Introduction.

Although the ionisation and excitation by low voltage electrons have been extensively studied experimentally, and the general course of these processes is fairly well mapped out, the phenomena of ionisation and excitation by slow positive ions have so far been but little attacked, and what experimental material exists is rather inconclusive.

The well-known formula for the current in a cumulative gaseous discharge was based upon the assumption that slow positive ions were capable of ionising the gas molecules they struck; and the accuracy with which this formula fitted the experimental results was taken as good evidence for the physical assumptions leading to it. But Holst and Oesterhuis* have suggested that in addition to the ionisation produced by the moving positive ions the secondary electron emission from the cathode produced by the impact of positive ions (a phenomenon otherwise demonstrable) plays an important rôle. This process, if it occurs, must render uncertain any quantitative conclusions as to ionisation by positive ions drawn from the classical formula.

Nor have direct electrical measurements of the ionisation led to any conclusive results. Pawlow's† early work was completely vitiated by the secondary emission mentioned above, and subsequent workers‡ have obtained only negative or inconclusive results. But recently Sutton, who used potassium ions at 100–700 volts acceleration potential, claims to have detected ionisation in neon and argon at these voltages. Oliphant (in an unpublished note)§ has, however, criticised his findings. Between his grids Sutton applies biassing voltages which are less than the ionisation potential of the gas used. He then assumes that the secondary electrons set free are incapable of ionising the gas.

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* 'Phil. Mag.,' vol. 46, p. 1117 (1923).

† 'Roy. Soc. Proc.,' vol. 90, p. 398 (1914).

‡ Horton and Davies, 'Roy. Soc. Proc.,' vol. 95, p. 333 (1919); Hooper, 'J. Franklin Inst.,' vol. 201, p. 311 (1926); Gurney, 'Phys. Rev.,' vol. 32, p. 795 (1928); Sutton, 'Phys. Rev.,' vol. 33, p. 363 (1929).

§ I am much indebted to Mr. Oliphant for directing my attention to this source of error.

But on account of their finite velocity of ejection this assumption is not necessarily true.

Dempster* was able to detect light in a canal ray beam in hydrogen at only 5 volts accelerating potential, but his experimental conditions were not arranged to give a single type of ion nor could he resolve spectroscopically the light so produced. The extraordinarily low voltages at which he observed the light suggests that the excitation occurs by some form of collision of the second kind.

The only certain results seem to be due to Tate† who has projected sodium ions with energies of 50 volts and upwards into mercury vapour. The spectra of sodium and mercury were excited, and this definitely proves ionisation of the mercury atom by capture of an electron into some state of the sodium ion, since the spectrum of sodium is emitted from a neutral atom. The method is independent of secondary electron currents.

This paper contains an account of experiments performed with a beam of slow sodium ions. Tate's results are verified ; and an account is given of some rough photometric measurements on the intensity-voltage relations of a group of mercury lines.

Repetition of Tate's Experiments.

1. A convenient source of positive ions is the ammonia-catalyst of Kunsman.‡ This source was used in the repetition of Tate's experiments. In place of platinum strip coated with sodium phosphate which he employed, a glowing tungsten spiral spread with a sodium or potassium source was used, and the ions, thermionically emitted, were projected through mercury vapour at about 0·023 mm. pressure into a field-free observation box. Accelerating voltages above 100 gave a faint glow in the observation chamber. The brightness of the glow increased considerably up to 400 volts, the highest potential employed, and under favourable circumstances it was possible, using a potassium source, to see the green spectral line of mercury at 400 volts accelerating potential. The light was yellow when sodium sources were used, and had apparently a purple cast with potassium sources.

Tate's results are therefore confirmed, but it was not possible to detect any light at 50 volts,§ though by using heavier gauge emitting filaments this would no doubt be possible, since there seemed no sharp limit to the illumination.

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* 'Phys. Rev.,' vol. 8, p. 651 (1916).

† 'Phys. Rev.,' vol. 23, p. 293 (1924).

‡ 'J. Franklin Inst.,' vol. 203, p. 635 (1927).

§ Since writing this paper an account has appeared of experiments in which, by increasing the time of exposure, it has been found possible to photograph λ 2537 of mercury down to 35 electron volts energy of the incident ion (Kirchstein, ' Z. Physik,' vol. 60, p. 184 (1930)).

Experiments with a Sharply-Defined Beam.

To obtain definite information on the intensity of primary light excitation a sharply-defined beam of positive ions should be used. This arrangement allows the primary excitation to be separated from light produced by stray arcing and by secondary electrons. Also, a directed beam allows one to see whether the emitted light is polarised.

A tube to give such a beam was therefore designed, and after it had been perfected it was found possible, using a source of sodium ions, to see the D lines of sodium through a spectroscope at only 200 electron volts energy of the incident ions.

The tube used is shown in fig. 1 (*a*) and (*b*). In its essentials it consists of a filament F which is maintained at a positive accelerating potential with respect to the slit P. The sodium ions, thermionically emitted from the filament pass through P and are collected in a cup C which serves to measure the current in the beam.

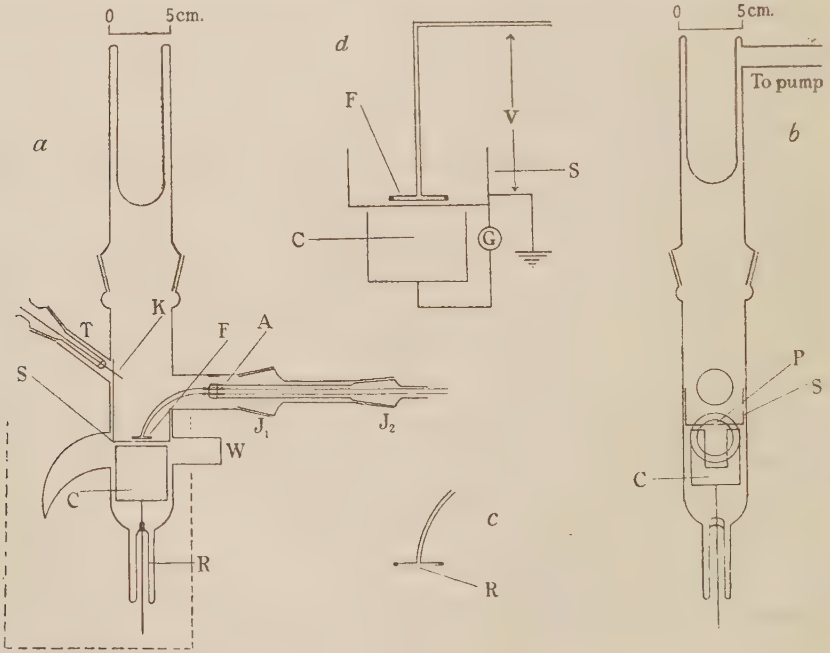

Fig. 1.

The main body of the tube which carried the electrodes was closed by a ground joint. Above this joint was a liquid air trap, as shown. A side tube from the trap led to a fast steel diffusion pump backed by a rotary mercury pump and a Fleuss oil pump.

The electrode system is shown likewise in fig. 1 (*a*) and (*b*). The body of the tube was divided into two parts by a disc of " staybrite " steel S, which carried the slit P. The disc was skirted, as shown, to prevent as far as possible leakage of mercury vapour from the lower part of the tube (the " high pressure side " of the slit) to the upper. The slit P in the earlier tubes was built up by welding and was about 1 cm. long and 1 mm. wide. Through it the positive rays enter the mercury vapour ; the luminous streak was viewed through a window W backed by a light trap as shown. The slit was woven across with wires of " staybrite " steel, otherwise at high accelerating voltages and high pressures the field from the filament leaked through it and started an arc on the high pressure side.

The collecting cup was of " staybrite " steel, cut as shown, so as to allow a view of the beam through W. It stood on a glass foot, through which the lead to the galvanometer passed. The external lead was suitably insulated from the water-bath through which it passed.

Connection from the plate S to earth was made by a dry contact between a wire K carried on the ground joint T and a sprig of wire welded to the plate.

The filament, fig. 1 (*c*), was a duct of platinum foil stretched between leads of " staybrite " wire doubled back, as shown, to minimise its stray magnetic field which might disturb polarisation measurements. The channel of platinum was filled with powdered Kunsman source, and heated in air before insertion so as to make the powdered source stick to the platinum.

The two leads curved up to the supporting pinch A which was carried on the double ground joint J_1 J_2. This device allows not only of to-and-fro motion of the filament across the slit, but also, since the axes of the two ground joints are not quite coincident the filament can be moved up and down to a certain extent with respect to the slit P. These motions can be performed while the tube is evacuated and are of great assistance in directing as much of the emission as possible through the slit.

The electrical connections are shown in fig. 1 (*d*), S is earthed, G is a galvanometer and the potential V accelerates the ions from F to S.

Attempts were first made to detect polarisation of the emitted mercury light. For this purpose the electrodes were annealed to make them non-magnetic, and the lower part of the tube could be immersed in a water-bath, shown dotted in fig. 1. A pellet of mercury in the lower part of the tube was the source of vapour. The filament was then coated and the joints greased with apiezon (a tap grease having a negligible vapour pressure), except the large joint at the top of the tube which was used dry and waxed on the outside with Everett's hard wax.

The high voltage which accelerated the ions was provided by a rectified transformer set* smoothed by a condenser. The filament was at a high potential with respect to the earthed slit P. It was heated from the insulated secondary of a transformer and its temperature could be varied by means of an insulated rheostat while the potential was still applied.

Before taking a run the tube was exhausted and the temperature of the water-bath raised to 60° C., giving a pressure at the lower side of the tube of 0·023 mm. mercury. The filament was then gradually heated, liquid air was poured in the trap and the high tension voltage was applied. In earlier experiments, before experience had been obtained with the tube, much trouble was experienced through a cumulative arcing which took place as soon as the filament began to emit. This arcing appeared to be due mainly to gas given off by the filament; by running the filament very hot for some time it was found possible to prevent it to a large extent. But since the life of the sources has been a great limitation on this experimental work it was found advisable to use a very fast pumping system which allowed the sources to be used while they had still their large initial emissivity. The megohm resistance prevented the arcing from blowing the fuses of the transformer.

This explosive arcing was also observed by Gurney (*loc. cit.*) in his experiments, but its mechanism is still obscure. Some observations suggest that it may be due to ionisation produced by secondary electrons liberated from the electrode S by the incident positive rays, since its occurrence seemed favoured by electrodes which were freshly replaced in the tube and in consequence heavily gassed.

Attempts to measure polarisation of the emitted mercury light in the same way as it was measured for electrons† gave negative results.

Exposures of between an hour and an hour and a half were given according to the life of the source. The work was very tedious on account of the necessity of recoating a filament for every exposure Accelerating voltages varied between 4,000 and 10,000.

The plates obtained showed only the lines λ 4358 and λ 3650 of mercury.

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* Thanks are due to Mr. de Bruyne and to Mr. Cockroft for their help in adapting the commercial transformer set used.

† Skinner and Appleyard, 'Roy. Soc. Proc.,' A, vol. 117, p. 224 (1927).

No consistent polarisation could be detected on these lines in this range of accelerating voltages. The polarisation cannot be greater than ± 4 per cent. for either of the lines under these circumstances.

It was not considered profitable to attempt the experiment at lower voltages on account of the difficulty of getting sufficiently intense beams. Instead, a rough determination of the efficiency-voltage curve for sodium ion impact was attempted.

Methods of Determining an Efficiency Curve.

Skinner and Lees* have pointed out the advantages of using a directed beam of exciting particles in order to study the intensity-voltage relations of spectral lines. In this method a beam of charged particles carrying a constant current is projected with varying velocity into the gas whose spectrum is to be studied. The intensities of the spectral lines so produced give a measure of the probability that the upper levels corresponding to these lines will be excited at the several velocities. An integrational method of photometry allows one to compensate (*a*) for light produced by secondary processes, (*b*) for change in the breadth of the beam as the voltage is varied.

Since the light emitted by positive ray excitation of mercury vapour is so faint, an approximate method of photometry had to be adopted. The beam was photographed directly through a slip of Crookes' glass using an ordinary camera working at F/4 and an Ilford Monarch plate. The Crookes' glass absorbs wave-lengths below λ 3500 (approximately), and so the lines which affect the plate are λ (3650, 3655, 3663), λ (4358, 4347), and the fainter lines λ (4047), λ (4078), etc. The sensitivity of the photographic plate is insufficient to give any appreciable effect with the green line of mercury, λ (5461). Also no lines of the principal series of sodium occur within this range, so that it is not likely that the sodium lines can contribute much to this intensity. Nor on the spectrograms at high voltages were there any signs of other spectral lines than those of mercury.

The way in which the intensity of this group of spectral lines varied with voltage was, therefore, found by approximate photographic photometry presently to be described.

For the efficiency measurements the positive ray tube was altered in several ways in accordance with experience.

The body of the tube and the liquid air trap were blown of pyrex. The platinum filament was replaced by an indirectly heated electrode (fig. 2). This consisted of a stout rectangular box B, of sheet molybdenum, which was heated by radiation from a glowing tungsten spiral S. Molybdenum was used on account of its great rigidity at high temperatures; with this construction much of the heat loss is by radiation, and the box could be made of fairly stout gauge. It was welded to one of two stout leads which were spaced by a bead of glass G fused to two sprigs of sealing-in wire, as shown. The tungsten spiral was carried on two thinner leads L of "staybrite" wire; the leads and the spiral were coaxial so as to facilitate centring. The spiral was thick tungsten wire ($\frac{1}{2}$ mm.) wound closely upon a 1 mm. mandrel, and the leads through the pinch A were made stouter to take the large heating current.

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* 'Nature,' vol. 123, p. 836 (1929).

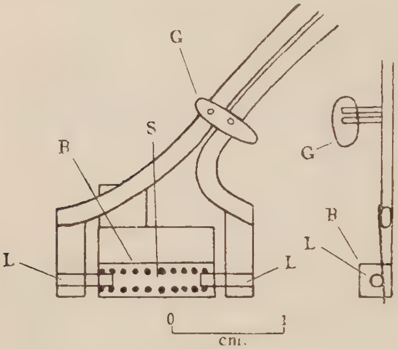

Fig. 2.

The cup C (fig. 1) was made deeper and the top, previously open, was partially closed leaving only a broad slit through which the ions from the slit P could enter. The bottom was slanted slightly to minimise loss by reflection of positive ions, and the geometrical spacing of the electrodes made more rigid by uniting S and C with long insulating rods of glass.

Connection to C from outside was made by a dry clip on the bottom of C which made contact with a tungsten wire sealed through the foot R (see fig. 1*a*). The electrical connections were as before. Since measurements were taken down to 100 volts a battery of dry cells replaced the high tension generator below 600 volts as the latter was unsatisfactory below this voltage.

A water-bath provided with a xylol thermostat and a stirrer determined the pressure of mercury vapour in the observation chamber. The pumping system was as before.

The source used in these experiments emitted sodium ions. It was prepared by grinding together very intimately iron oxide with about 1 per cent. of NaOH, sintering the mixture at red heat, and again re-powdering. It seemed to be of some advantage to repeat the powdering and heating so as to get a more uniform mixture. In order to improve the emissivity of the source it may be reduced in hydrogen. For convenience the reduction was performed in bulk by heating the powdered source to a bright red heat in a stream of hydrogen. Half-an-hour's reduction was usually sufficient. The grey powder of metallic iron was worked up to a paint with xylol and spread on the lower face of the molybdenum box. Several coats were applied to give a good thickness (1 mm.)

of emitting material and the vehicle was subsequently dried off in the current of hot air over a bunsen.

In addition to having a superior emission the source when reduced sticks better to the emitting electrode once it has been heated to redness, and being a good conductor of heat it appears to heat up more uniformly over its whole surface.

Recapture Light of Sodium.

Before describing the photometric methods in detail it is of interest to consider the light given out by the sodium atoms in the beam. With the new form of tube it was found possible to view the beam at very low pressures of mercury vapour. After exhausting the tube and putting liquid air in the trap the filament was adjusted by means of the ground joints to give a maximum current in the beam when a suitable accelerating voltage was applied. The beam was then visible at currents of 30 to 40 microamperes as a bright yellow streak at the pressure of mercury vapour corresponding to room temperature. The beam seemed to show no great variation of intensity along its length.

On this account it seems likely that the greater part of the sodium light is emitted by recapture of an electron from a mercury atom into some excited state of the sodium atom.* For if the light were emitted by recapture into a ground state of the sodium atom with subsequent excitation and emission at a second collision with a stationary mercury atom the intensity of emission of the D lines, say, should be proportional to the number of neutral atoms at a given point in the beam. This number will be small where the beam enters the high pressure side, for the positive ions will have made few collisions between the filament and the slit, and it should increase rapidly as we move along the beam. Assuming a mean free path† for the sodium ion of 6 cm. in mercury vapour at room temperature, a rough calculation shows that the light should increase about three times in intensity as we move from 2 mm. to 1·2 mm. from the slit along the beam. A variation as large as this could be detected visually if it occurred.

The result may be compared with the experiments of Mohler‡ on recapture of free electrons into the excited states of the alkali metals. He found from a measurement of the intensity of the continuous spectrum emitted by this process that recapture into the $2\,^2P_{\frac{3}{2},\frac{1}{2}}$ states of caesium was much more probable than capture into the ground state.

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* The sodium light in this case will still show a sharp initial rise due to the finite half life of the excited state. For the velocities used this sharp rise would occur along the initial few millimetres of the path, and in the apparatus described would take place for the most part between the filament and the slit. Any rise occurring in the observation box, after the beam had entered the high pressure side, would be hard to detect if it occurred within a millimetre or two of entry on account of the brightness of the slit edges caused by light from the filament.

† Calculated on the assumption of a radius for the sodium ion equal to that of a neon atom under gas-kinetic conditions.

‡ 'Phys. Rev.,' vol. 31, p. 187 (1928).

The suggestion also accounts simply for the old experiment of Reichenheim,* where a beam of light-emitting sodium ions was deflected as a whole by a crossed electric field. It seems simpler to account for this behaviour on the assumption given above rather than to assume abnormally short free paths for the sodium neutral atoms before they become excited.

Voltage-Intensity Relations.

The camera used to photograph the beam worked at an aperture of about F/4. It was fixed so as to give a magnification of about one-third in the final series of exposures. Three exposures could be taken on a single plate.

In taking a run the water-bath was raised to the appropriate temperature, the filament was run until it had been outgassed, and until any mercury droplets had distilled from S to the liquid air trap. On applying a suitable accelerating voltage there was usually a measurable current in the beam as registered by the galvanometer G. By adjustment of the filament, using J_1 and J_2, the maximum current obtainable at a given filament temperature was put through the slit, and the emission was then increased until it had reached a value considerably exceeding the final value it was proposed to use in the run. This overheating rendered the subsequent emission steadier. A current of about 5 microamperes was used in the main beam. The voltage was now raised to an appropriate value as read on a Braun voltmeter of suitable range. The exposure was then taken.

Ten-minute exposures were used and it was found possible to take a series of five exposures from one filament. The plates were then developed under standard conditions in a tank in which the developer could be violently agitated.

The current in the beam was kept as constant as possible and was read at regular intervals so as to obtain an average. The intensity curves which are published were all from exposures taken at a pressure of about 0·0024 mm. Hg as determined by the water-bath.

The Photometric Methods.

In order to compare the intensities which have produced definite blackenings on a photographic plate it is necessary to calibrate the plates used by means of a series of exposures of graded intensities which are developed under the same conditions as the plates to be compared. The comparison is here complicated by the fact that the light is heterochromatic, and the quality is not accurately known.

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* 'Z. Electrochem.,' vol. 16, pp. 583–585 (1910).

In the reduction of blackenings to intensity the following method was therefore adopted.

The plates were calibrated for 10-minute exposures by the method of slit-width variation at the wave-lengths λ 4358 and λ 3650. The ratio of the intensities producing two different blackenings can be read off first from one curve and then from another; and if the curves have the same shape the ratios so obtained should be the same. In any case, provided the two lights have the same quality the two ratios so obtained will bracket the extreme limits of photometric error from this cause.

In obtaining these curves a "Fullolite" opal lamp was focussed on the slit of the spectrometer (a large Hilger quartz spectrograph) and 10-minute exposures were given. Different currents were used in the lamp for the two wave-lengths since the intensity of the continuous spectrum varies a good deal in passing from one wave-length to the other. The voltage across the lamp was kept constant as recommended by Dobson, Griffiths and Harrison.*

To allow for the variation in the shape of the beam at different voltages the integrational method used by Skinner and Lees (*loc. cit.*) was adopted. The density of the photographic plate was measured at various points across the image of the beam where it entered the Faraday cylinder. The corresponding intensities were read off from the calibration curves, and a curve was plotted, intensity against distance across the beam. An experimental curve is shown in fig. 3. It will be seen that the secondary excitation is small.

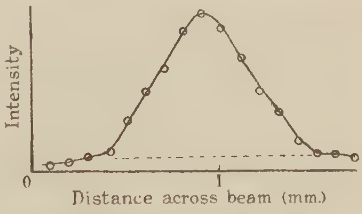

Fig. 3.—1000-volt beam.

The area under the hump divided by the appropriate current then gives a measure of the probability of excitation at this voltage. This quantity was found by averaging ordinates and dividing by the appropriate current at the different voltages. Both calibration curves were used to reduce the densities and the resulting measures of the efficiency were plotted on two separate curves against voltage.

There remains still another source of error in the photometry. The line groups λ (3650, 3653, 3663) and λ (4347, 4358) may not increase in the same ratio as the voltage varies, *i.e.*, the "colour" of the light may change with voltage, so that the intensities previously obtained do not represent the actual variation of intensity of the total light in this line group. Preliminary rough experiments had shown that the general character of the variation of λ (4358, 4347) was similar to the variation for the whole group. This was done by passing the light from the beam through a filter of potassium chromate solution which strongly absorbs the group λ 3650, leaving the group λ (4358, 4347) practically unaltered. But because of the absorption of the cell it was found very difficult to obtain sufficient photographic density from the resulting filtered radiation and it seemed at first impracticable to obtain numerical results. Nevertheless the general character of the variation was the same, and the dotted curve in fig. 4 shows such rough results as were obtained. The filtered and the unfiltered curves are fitted together to have the same initial ordinate.

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* "Photographic Photometry" (Oxford, 1926).

The Experimental Results.

The results for the final series of exposures of the low pressure series are shown in figs. 4 and 5.

In order to get the more representative series of results the intensities from the low pressure series of runs are assimilated to one curve. In fig. 4 two series at high voltages are plotted on one curve, reduced to the same mean ordinate. Each voltage has four points because the ordinate in any series at a definite voltage is read off both from the λ 4358 plate calibration and from the λ 3650. The resulting curve uses all the results and is probably most representative of the variation. Fig. 5 is a series taken at low voltages. The intensity for 100 volts is a little uncertain because of the difficulty of getting a current of 5 microamperes through the slit at the low voltages; all that can be said is that the excitation is small.

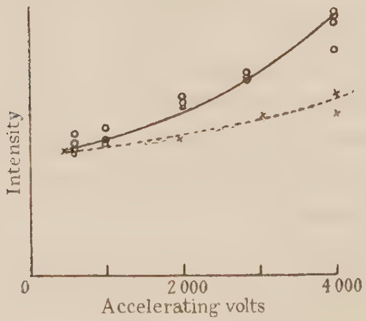

Fig. 4.

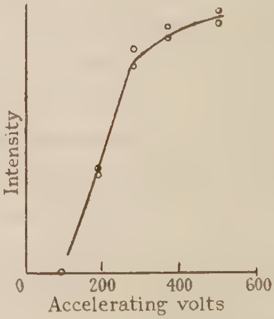

Fig. 5.

It will be noted that for the filtered radiation the ratio of the ordinates at 4000 volts to the ordinate at 600 volts is 1·4 : 1, the ratio for the unfiltered is 2 : 1. The error in the unfiltered curve due to the change in colour of the light is therefore probably 30 per cent. at most of the ratio of any two ordinates. Hence no great claim is made for the numerical accuracy of the results; all that can be said is that both line groups show a sharp initial rise of intensity with increasing voltage to about 400 volts and a subsequent slower increase.

Other sources of error are less important. Secondary electrons from the edges of the slit may stray from the cup C and contribute to the measured current. A magnetic field was applied across the tube in order to eliminate this effect. To estimate the effect produced by straying of ions from the cup the latter was biassed with different voltages, until saturation was attained. The change in current amounted to about 10 per cent. of the original primary current. Without an accelerating field the error from this cause will be much less.

Positive rays of mercury may also be produced by ionisation between the slit and the filament as the secondary electrons pass through the mercury vapour. On account of the short distance between slit and filament (2 mm.) the amount of this type of ionisation cannot have been large. A rough estimate gives it as 0·8 per cent. of the electron current.* Since primary positive ion and electron current are of the same order the error on this account cannot be large, unless the mercury positive ions are very much more efficient than the sodium positive ions in exciting light.

Discussion.

Joos and Kulenkampff† have shown that the energy and momentum relations allow excitation of a neutral atom by a massive particle, provided the energy of the incident particle exceeds $W_0(1+\eta)$, where W_0 = energy of excited atom, and η = the ratio of the incident to the struck mass. About the efficiency of the process the energy and momentum relations say nothing, and it is clear from fig. 5 that if excitation of the lines λ 4358 and λ 3650 does occur below 100 volts it must be very slight between the critical voltages of these two lines for sodium ion impact (8·6 and 9·85 volts) and 100 volts.

The behaviour of positive ions is in striking contrast therefore to that of electrons under the same circumstances. For electrons the efficiency of excitation rises sharply to a maximum at about 3 volts above the critical potentials for these two lines of mercury.* And if we compare the efficiency, not at corresponding energies but at corresponding velocities, there is no better agreement, since these positive ion velocities are much less than any electron velocities which excite (5×10^6 cm. per second for a 400-volt sodium ion, $1 \cdot 5 \times 10^8$ cm. per second for a 9-volt electron).

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* Estimated from the ionisation measurements of Compton and Van Voorhuis 'Phys. Rev.,' vol. 26, p. 436 (1925).

† 'Phys. Z.,' vol. 25, p. 258 (1924).

A detailed theoretical treatment of the collision of a positive ion with a neutral atom does not yet exist, but Born and Elsasser† have applied the methods of the wave mechanics to a consideration of the excitation of the several levels of atomic hydrogen by a particle repelling with an inverse square law of force. Their treatment is approximate and may not be adequate at the velocities here considered. In fig. 6 Elsasser's formula has been used to calculate the efficiency of proton excitation in atomic hydrogen. Abscissæ are proportional to the voltages marked, ordinates are efficiencies in terms of

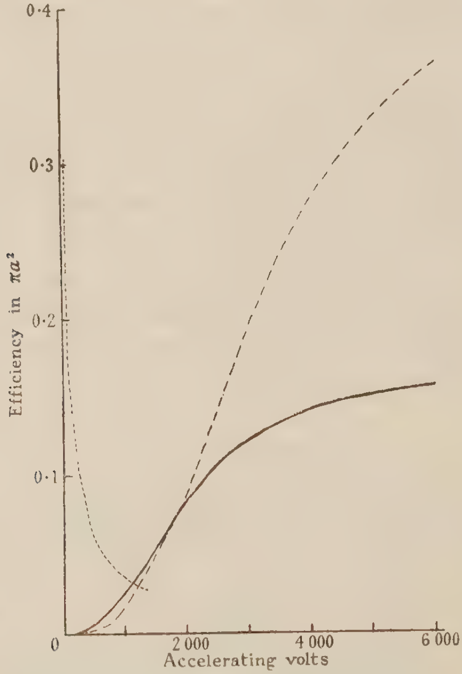

Fig. 6.—(The electron efficiencies are drawn half scale.)

------ Proton ϕ (2,0). –·–·– Proton ϕ (2, 1).
.... Electron ϕ (2, 1).

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* White, 'Phys. Rev.,' vol. 28, p. 1125 (1926).

† Born, "Göttinger Nachrichten," p. 146 (1926); Elsasser, 'Z. Physik,' vol. 45, p. 152 (1927). Elsasser's notation is here used.

πa^2, the target area of the first Bohr ring. The curves refer, as shown, to excitation of the two components of the resonance line of hydrogen; for all lines of hydrogen the curves will have a similar general shape.

A comparison with figs. 4 and 5 shows that the curves have the same general character, giving a low efficiency at low voltages followed by a sharp rise and a subsequent bending over at an intensity of the same order as the maximum efficiency for electron impact. The intensity experimentally found for positive ray impact could only be compared with electron efficiency by approximate estimation of the photographic blackening. From experience with electron tubes, positive ray and electron efficiencies at their maximum appear of the same order. For sodium ion impact, however, the initial rise experimentally found is much sharper than that calculated.

Nevertheless it may be said that in a general way Elsasser's formula accounts for the differences observed between electron and positive ion impact. The comparison must be made with due reserve because Elsasser's treatment of an excessively idealised case cannot be applied without danger to an incident particle whose field is complicated, and distorted during the collision, and to lines of different spectral type. The treatment also neglects resonance effects and spin couplings between the exciting and the orbital electrons, and so may require modification for electron impact.

No measurements were made of the efficiency of electron capture by the sodium ion. This process, like the excitation of the mercury spectrum, involves the transformation of kinetic energy into energy of excitation, for the ionisation potential of mercury is larger than that of sodium. But since it occurs when the energy of the ion is only 100 electron volts it appears to offer a promising method of testing whether kinetic energy is handed over to the struck particle.

For high velocities of the incident ion the transfer is not detectable.* This behaviour is comprehensible as Joos and Kulenkampf (*loc. cit.*) point out in their paper.

In excitation the orbit of the series electron is powerfully distorted by the field of the positive ion and is moved to an outer orbit. In the distorting process it reacts by its binding force upon the core and momentum will thereby be transferred to the core, the amount depending upon the impulse of the forces. At high velocities the time of excitation is small, and the impulse therefore small, so that not much momentum will be handed over by this process. It is more hopeful therefore to look for energy transfer at low velocities.

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* Wien, "Kanalstrahlen," p. 238 (Leipzig, 1923).

The momentum relations give, when generalised for scattering at any angle,

$$\mathrm{E} = \mathrm{E}_0 \frac{\eta}{(1+\eta)^2}\left[\cos\theta \pm \left\{\cos^2\theta - \frac{\mathrm{W}}{\mathrm{E}_0}(1+\eta)\right\}^{\frac{1}{2}}\right]^2 .$$

In this formula E is the kinetic energy transferred to the struck particle, E_0 is the energy of the incident ion, W is the energy of the excitation process and η is the ratio of the incident to the struck mass. θ is the angle which the velocity of the recoil particle makes with the original direction of the incident ion. If an ion of caesium with energy of 100 electron volts enters mercury vapour this formula gives for the energy of a mercury ion so produced, recoiling at an angle of 30° and produced by capture of an electron into the $2\,{}^2\mathrm{P}_{\frac{3}{2},\frac{1}{2}}$ state of caesium, 0·20 or 66·3 volts, which should be easily detectable.

Summary.

Experiments are described on the light of recapture of sodium ions in mercury. It is concluded that there is no evidence for any type of ionisation by slow positive ions except ionisation by capture (probably into an excited state) which is detected optically. This leaves open the question of the rôle of the positive ion in the gaseous discharge. An approximate efficiency-voltage curve for the line groups λ (4358, 4347) and λ (3650, 3655, 3663) of mercury is obtained and compared with the efficiency-voltage curve for electrons.

I take here the opportunity of thanking the various members of the Cavendish Laboratory, who have given me assistance during the investigation by advice and conversation. In particular I must thank Mr. P. M. S. Blackett, who has continually encouraged me and has given me numerous suggestions; Mr. Oliphant, for conversation and for advice in the preparation of the sources; and Dr. H. W. B. Skinner, now in Bristol, for various details of experimental technique and for discussion.

Thanks are also due to Prof. Sir Ernest Rutherford, who has taken a continual interest in the progress of the research, and to the Department of Scientific and Industrial Research, for a grant which made this work possible.

The Absorption of Hard Monochromatic γ-Radiation.

By G. T. P. Tarrant, B.A., Pembroke College, Cambridge.

(Communicated by Sir Ernest Rutherford, P.R.S.—Received May 5, 1930.)

Introduction.

Energy may be removed from a beam of γ-rays traversing matter by two distinct mechanisms. A quantum of radiation may be scattered by an electron out of its initial direction with change of wave-length, or it may be absorbed completely by an atom and produce a photoelectron. The total absorption coefficient, μ, is defined by the equation

$$\frac{dI}{dx} = -\mu I,$$

and is the sum of the coefficients σ and τ referring respectively to the scattering and to the photoelectric effect.

For radiation of low frequency, such as X-rays, the photoelectric absorption is very much more important than the absorption due to scattering, and many experiments have shown that the photoelectric absorption per atom varies as the fourth power of the atomic number and approximately as the cube of the wave-length. For radiation of high frequency, such as the more penetrating γ-rays, the photoelectric effect is, even for the heavy elements, smaller than the scattering absorption; and, since the scattering from each electron is always assumed to be independent of the atom from which it is derived, it is most convenient to divide μ defined above by the number of electrons per unit volume in the material and to obtain μ_e the absorption coefficient per electron.

The formula proposed by Compton to give the change of wave-length of the rays scattered at any angle only defines the energy and momentum relations in the scattering process, and is established on definite experimental evidence. The probability with which this scattering process occurs is not yet definitely known, for, owing to the difficulty of isolating a γ-ray of high frequency, the experimental evidence is not sufficiently precise. Various formulæ have been proposed to give the intensity of a radiation of original frequency ν scattered by an electron through any angle, and, by integration, the magnitude of the scattering coefficient per electron, σ_e. The most important relations for the scattering coefficients are :—

Compton*

$$\sigma_e = \frac{8\pi e^4}{3m^2c^4} \frac{1}{1+2\alpha};$$

Dirac†

$$\sigma_e = \frac{2\pi e^4}{m^2c^4} \left\{ \frac{1+\alpha}{\alpha^2} \left[\frac{2(1+\alpha)}{1+2\alpha} - \frac{1}{\alpha} \log_e (1+2\alpha) \right] \right\};$$

Klein and Nishina‡

$$\sigma_e = \frac{2\pi e^4}{m^2c^4} \left\{ \frac{1+\alpha}{\alpha^2} \left[\frac{2(1+\alpha)}{1+2\alpha} - \frac{1}{\alpha} \log_e (1+2\alpha) \right] + \frac{1}{2\alpha} \log_e (1+2\alpha) - \frac{1+3\alpha}{(1+2\alpha)^2} \right\};$$

where $\alpha = h\nu/mc^2$.

The formula found by Klein and Nishina, which is based on wave-mechanics, has been calculated from that proposed by Dirac with the inclusion of relativistic corrections. These formulæ all become identical in the X-ray region, but for hard γ-rays the value of the absorption coefficient calculated from the Klein and Nishina formula is about double that obtained from the others.

In many cases, for example, in the case of the penetrating radiation observed in the atmosphere, estimates of the wave-length of a radiation are based on measurements of the absorption coefficients, and very different values are obtained according to which of the theories of scattering is adopted. It was to test the accuracy of these theories of scattering that the experiment described in this paper was commenced, by measuring carefully the absorption of a large number of elements for a practically homogeneous γ-radiation of very high frequency. The results of this work show that the formula for the scattering coefficient σ_e given by Klein and Nishina is accurate to within the limits of the experiments for a number of the elements listed. In a few elements, however, the absorption shows a marked abnormality for which no theory of absorption yet advanced offers any explanation, and which may perhaps be due to an interaction of the high frequency γ-rays with the nucleii of these elements.

In all measurements of the absorption of energy from a beam of γ-rays the scattering of the rays is of the utmost importance, because the value of the absorption coefficient obtained is affected by the scattered rays which enter the ionisation chamber. Owing to the change in wave-length and in ionisation function of the scattered rays, the corresponding correction to be applied is only calculable with accuracy when the half-angle subtended by the chamber at the source is small—about 1°. Since this condition has made it imperative to employ very large sources experimenters have, hitherto, used radium (B+C). The greatest difficulty is experienced in the interpretation of the results of absorption measurements with such sources, for the rays emitted from radium (B + C) are very complex, and have energies ranging between $0 \cdot 2$ and $3 \cdot 0 \times 10^6$ volts. A partial separation of the soft and hard rays may be effected by filtering, but even the best filtered beam still contains a very considerable mixture of rays. The best values obtained are thus averages of the general type :—

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* ‘Phys. Rev.,’ vol. 21, p. 483 (1923).

† ‘Roy. Soc. Proc.,’ A, vol. 111, p. 405 (1926).

‡ ‘Z. Physik,’ vol. 52, p. 853 (1929).

$$\mu = \frac{1}{a} \log_e \frac{I_1 k_1 e^{-\mu_1 x} + I_2 k_2 e^{-\mu_2 x} + \text{etc.}}{I_1 k_1 e^{-\mu_1 (x+a)} + I_2 k_2 e^{-\mu_2 (x+a)} + \text{etc.}},$$

where I_1, I_2, etc., represents the initial intensities of the γ-rays, k_1, k_2, etc., are the ionisation constants representing the relative ionising power of the different wave-lengths, x is the thickness of the filter and a that of the absorber.

In the experiment described in this paper the absorption coefficient of the high energy γ-ray emitted by thorium C″ has been measured to an accuracy of 1·2 per cent., after it had been isolated from the softer components by filtering through lead. This filtering is best explained by the following table, which gives an estimate of the absorption coefficient in lead of the more penetrating γ-rays found by Black to be emitted by a source of radiothorium in equilibrium with its disintegration products.

Table I.

Energy of γ-ray in 10^6 volts.	Source.	Absorption coefficient in lead cms.$^{-1}$.
2·649	Th C″	0·45
0·658	Th C″	1·1
0·5176	Th C″	1·51
0·2998	Th B	4·1
0·2916	Th C″	4·36

From this table it is seen that the hard ray can be isolated from the rest by filtering through a suitable thickness of lead, which was found experimentally to be about 3 cm. This filter thickness was not expected to be very great, since Bastings has estimated from Black's data that 70 to 80 per cent. of the energy is in the hard ray.

Experimental Arrangement.

Since the available source of radiothorium and its products was small, having a γ-ray activity equivalent to that of 10·5 mgs. of radium, attention had to be paid to those methods of increasing the sensitivity of the apparatus and the effective strength of the source, which would leave unaffected the purity of the rays and the interpretation of the experiment. In the usual arrangement of apparatus the source, filter, absorber, and ionisation chamber are placed at equal distances from each other. The effective strength of the source has here been increased by placing the filter directly in front of the chamber and so diminishing the distance between chamber and source.

At large filter thicknesses the absorption coefficient measured will then refer to the hard ray, since it alone can penetrate the filter. The ionisation in the chamber will be increased since those hard rays which are absorbed are largely rescattered in the forward direction where they will have a larger ionisation function. Another advantage of the arrangement is that the rays passing through the absorber are quite pure and free from degeneration by the filter. This disposition of the filter would be a disadvantage for radium where there is a continuous distribution of γ-rays and where there is no possibility of obtaining a single monochromatic ray.

The apparatus employed is shown in fig. 1. The rays from the source pass through the absorber, then through the filter and reach the ionisation chamber,

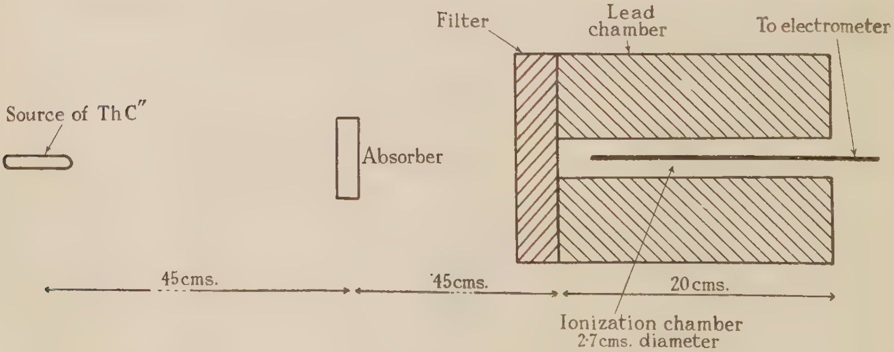

Fig. 1.

where the current is measured by a Compton electrometer (sensitivity 7000 mm. per volt). Use was made of the Townsend compensation method in which the electrometer system is maintained at a constant potential by inducing an opposite charge on a balancing condenser.

The lead walls of the ionisation chamber were 6 cm. in thickness to reduce the effect of radiation scattered from objects in the room. In order to increase the magnitude of the effect the chamber was lined with old lead instead of aluminium. This weights the soft rays very much more than the hard, so that a larger filter thickness was used than would otherwise have been necessary.

Only rays which are scattered at small angles will affect the value of the absorption coefficient obtained at large filter thicknesses, since the change in wave-length of the hard ray when scattered through large angles is so considerable that it must be completely absorbed in the filter. For this reason no lead canalising system was used round the source, which was mounted on a light wooden holder a foot above the table so that no radiation scattered in the forward direction by the table would pass through both the absorber and the chamber. In this experiment, therefore, the radiation which passes through the absorber and then enters the chamber is quite uncontaminated with any slightly softer scattered radiations.

The absorbers were hung by a light silk thread from a large wooden scaffolding. They could be replaced accurately in the standard position by means of a system of sighting through holes in the wood at the back of the source. Wooden frames were made to fit both the scaffolding and the absorbers and were of value in replacing the absorber in position.

Mode of Measurement.

The natural leak of the electrical system was rather large (10 per cent. of the direct effect) owing to the ionisation of the air in the electrometer guard tubes and chamber by the radiation scattered from the walls of the room. It was measured by placing in the position usually occupied by the absorber a long lead block of the same diameter, and on each day as much care and attention was bestowed on the natural leaks as on the other quantities. If the filter thickness be large enough, the effect produced in the chamber is directly proportional to the intensity of the hard rays, and

$$\mu = \frac{1}{a} \log_e \frac{\mathrm{I}_0 - \mathrm{I}_{\mathrm{Leak}}}{\mathrm{I} - \mathrm{I}_{\mathrm{Leak}}}.$$

The current due to the γ-rays was of the order of 4×10^{-15} amp., and corresponded in general to the transfer of about 7×10^6 ions in from 2 to 6 minutes. With these very small currents the effect of any α-particle contamination is very disturbing; and a slight contamination is unavoidable in this laboratory. Consequently a large number of measurements had to be taken for each ionisation current in order to obtain a reliable mean.

The value of each ionisation current involved in the measurement of an absorption coefficient was the mean of from 6 to 10 separate observations. The order in which these quantities were taken was varied, and a bracketing method frequently employed, in order to eliminate systematic error. The final value of the absorption coefficient for each element was the mean of from 7 to 12 of these separate determinations, and was therefore the result of from 60 to 120 separate measurements of each of the three quantities involved.

The probable error in each of the separate values of the absorption coefficient was deduced from the variations of the separate measurements of the current. For one element a probability curve was constructed out of about 200 readings and this agreed as well as might be expected with the theoretical curve, showing that the individual variations obey a probability law.

The probable error in the final result for each element was deduced from the variations in the separate values of the absorption coefficients. It agreed with the error calculated from the variations of the individual currents, thus showing that there was very little error in adjusting the position of the absorbers.

The Absorbers.

In the earlier measurements the absorbers were cylinders of from 4·8 to 5·0 cm. diameter, and of such a thickness that they reduced the intensity of the beam by about 33 per cent. The value of the absorption coefficient obtained is then very sensitive to errors in the ratio of the two currents, so that to obtain absorption coefficients accurate to 1 per cent. the current ratio must be known to 0·3 per cent. In the later measurements the absorbers were, therefore, made somewhat thicker. This change will not affect appreciably the relative values at 3·2 cm. filter thickness, because the filter curves shown in fig. 2 are flat in this position, and because the correction for the soft component is calculated for each individual absorber.

The first absorber to be made was of lead, and no attention was paid to its purity. On analysis it was found to contain only 82 per cent. of lead, and the measurements were therefore repeated with a pure specimen. The absorption coefficients given in Table V under the heading "Impure lead" have been corrected for this impurity, so that they are directly comparable with the measurements for pure lead.

After this, considerable care and attention were paid to the purity of the specimens employed. The purest specimens available were used; a density determination was invariably carried out, and whenever possible a chemical analysis of the material was made.

The effect of impurity was eliminated still further by determining μ/ρ and not μ, using the mass per square centimetre and not the length. Errors due to impurities are then due to variations in the assumed number of electrons in unit mass, and thus to the slight variations of Z/A with atomic number. Hydrogen is, therefore, the most objectionable impurity, since the ratio Z/A is roughly the same for all other elements.

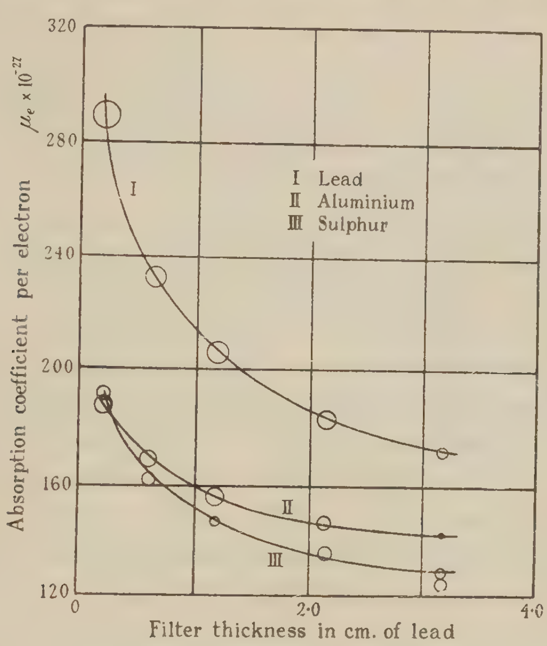

Fig. 2.

The sodium was cast in a glass cylinder and the glass then cracked off. It was too soft to be turned but was rolled and moulded till quite cylindrical. The block was kept in dry air and the thin layer of oxide which formed on the surface was wiped off each day before taking measurements. Due to this decomposition its dimensions changed slightly from day to day.

The percentage of hydrogen in paraffin wax was determined from a knowledge of its melting point which corresponded to $C_{26}H_{54}$, or to 14·76 per cent. of hydrogen.

The percentage of hydrogen in the carbon used (Acheson graphite) was obtained from the published analyses. Owing to the small changes in Z/A for the other elements any other possible impurities may be neglected.

The Scattering Correction.

The elements were measured at the greatest convenient filter thickness, viz., 3·2 cm. of lead. To obtain the true value of the absorption coefficients of the hard ray, these values need correcting slightly for the scattered rays which enter the chamber in spite of the small angle it subtends, and for the small amount of soft component which penetrates the filter. Only the first of these will be considered at this point.

The measurements described in this paper prove that the absorption formula of Klein and Nishina is valid within the limits of the experiment. Since the absorption formula is obtained by integration of their expression for the angular distribution of the scattered rays it is justifiable to use the latter to find the small correction for the scattered rays; but, as a check, a rough experimental method was devised in which the absorption coefficient was measured in absorbers of varying diameter. This check agreed as well as might be expected with the formula, although the individual measurements were only accurate to about 2 per cent.

The absorbers were placed half way between the source and the chamber, for a crude calculation had shown that the scattering correction would be least in this position. The half angle subtended at the centre of the absorber by the chamber was 1·73°, and a calculation based on the Klein and Nishina formula shows that the correction for the scattered rays is then 1·0 per cent. ± 0·2 per cent., and is almost independent of the thickness of the absorbers.

Variation of the Absorption Coefficient with Filter Thickness.

A knowledge of the variation of μ_e with filter thickness is necessary in order to find the correction due to the small amount of soft radiation still present at 3·2 cm. Furthermore, at this thickness, the values of the absorption coefficients per electron for certain elements, *e.g.*, aluminium, were found to be markedly different from those found for carbon, sulphur, etc.; and in order to determine if this is a spurious effect or if it is a real phenomenon connected with the high quantum energy of the hard ray concerned, it is important to discover if the difference in the absorption coefficients of these elements varies as the filter thickness diminishes and as the softer component begins to predominate.

To facilitate comparison, the experimental values of $\mu_e \times 10^{-27}$ for the various elements are tabulated below, after the correction for scattering has been applied.

Table II.

Filter thickness, cm. :	0·2.	0·61.	1·17.	2·15.	3·17.
Pure lead, $\mu_e \times 10^{-27}$	289·3	234·6	207·0	182·4	171·4
Aluminium, $\mu_e \times 10^{-27}$	187·2	168·3	151·9	146·4	142·0
Sulphur, $\mu_e \times 10^{-27}$	191·9	161·3	146·6	135·4	124·4
Mean value of a number of elements					128·8

The difference between the absorption coefficients of the radiation in aluminium and in sulphur diminishes as the intensity of the soft component increases relative to that of the hard ray. This suggests that the phenomenon is a characteristic of the large quantum energy of the γ-ray concerned. The curves showing the variation of the absorption coefficients with filter thickness are plotted in fig. 2, where the radius of the circles indicates the probable error of the experimental values. The intersection of the curves is due to the differences in the number of absorbing electrons in each absorber.

It is necessary to deduce the absorption coefficient of the soft rays in the filter in order to show that all three of these curves are really compatible with each other, when the differences of relative thicknesses are considered. For this purpose let the absorption coefficients of the hard and soft component of the rays be μ' and μ'' in the absorber and F′ and F″ in the filter respectively. Then, if the ionisation produced by the soft component is initially S times that of the hard component, and a is the thickness of the absorber and x of the filter, the observed absorption coefficient μ is :—

$$\mu = \frac{1}{a} \log_e \frac{e^{-\mathrm{F}'x} + \mathrm{S}\,e^{-\mathrm{F}''x}}{e^{-\mathrm{F}'x} e^{-\mu' a} + \mathrm{S}\,e^{-\mathrm{F}''x} e^{-\mu'' a}}.$$

From this it can be proved that

$$(\mathrm{F}'' - \mathrm{F}')\,x - \log_e \mathrm{S} = \log_e \left\{ \frac{1 - e^{-(\mu''-\mu')a} e^{+a(\mu-\mu')}}{e^{a(\mu-\mu')} - 1} \right\}.$$

Denoting the expression on the right-hand side by F (x), the slope of the straight line obtained by plotting this function against x gives the value of (F″ − F′) in the filter. The lines are not altered greatly by changing the value of $(\mu'' - \mu')$ assumed ; in the case of lead this may be obtained by a series of approximations, and for the other elements can be obtained sufficiently accurately from the wave-length of the soft rays and the Klein and Nishina formula.

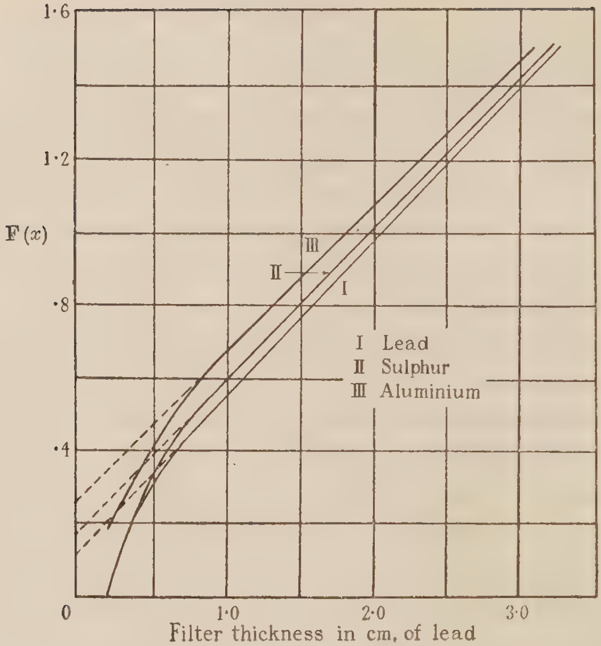

Fig. 3.

The values of this function for different values of x are shown in fig. 3 and in the following table.

Table III.

x, cm. :	0·2.	0·5.	0·8.	1·1.	1·4.	1·7.	2·0.	2·3.	2·6.	2·9.
F (X) for lead	$\bar{1}$·987	0·287	0·443	0·568	0·693	0·825	0·951	1·085	1·259	1·356
F (X) for aluminium	0·179	0·396	0·574	0·703	0·822	0·935	1·061	1·154	1·258	1·340
F (X) for sulphur	$\bar{1}$·971	0·308	0·493	0·632	0·738	0·876	1·002	1·149	1·255	1·348

The values of $(\mu_e'' - \mu_e')$ assumed were 366·0, 143·0, 143·0 × 10^{-27} from lead, aluminium and sulphur respectively.

These curves are all straight lines except near the origin, where their curvature is due to the presence of a third and very much softer component which is completely absorbed in 0·7 cm. of lead. This corresponds to the known γ-rays of quantum energy less than 0·3 × 10^6 volt. The fact that the lines are not all coincident is due to experimental error, since an error in the observed absorption coefficient of 2 per cent. makes a difference in the function of 0·07. The values of $(F'' - F')$ deduced from these curves are as follows ;—

Table IV.

Absorber.	Lead.	Sulphur.	Aluminium.
S	0·79	0·69	0·56
(F″ − F′), cm.$^{-1}$	0·98	0·97	0·87

The mean values of S and of (F″ − F′) are therefore 0·68 ± 0·05 and 0·94 ± 0·03 cm.$^{-1}$ respectively.

After passing 3·2 cm. of lead the intensity of the soft component is 0·034 ± 0·005 times that of the hard component. Using this, and assuming reasonable values for the two absorption coefficients, the correction for the soft component may be deduced for each element and is tabulated with the values for the absorption coefficients of the various elements. It may be considered to have a probable error of 0·3 per cent. due to uncertainty in the amount of the soft component present at 3·2 cm. filter thickness, and 0·3 per cent. due to the uncertainty as to the values of its absorption coefficient in each absorber.

The filter curves are also of importance in that they show that the photo electric absorption is not accurately proportional to the cube of the wavelength. If this rule held, the value of the absorption coefficient of the soft component would be 1·13 cm., whereas the experimental value of the absorption coefficient is 1·4 cm., and since the filter was placed immediately in front of the ionisation chamber this figure must be considered as a lower limit.

Significance of the Results.

In Table V are presented the values of the absorption coefficients of the hard thorium C″ γ-rays (2·649 × 10^6 volts) in a number of elements calculated directly from the experimental data. The final corrected value of μ_e includes the uniform correction of 1 per cent. of the scattered radiation entering the ionisation chamber, and the varying correction shown in the preceding column which allows for the small amount of soft component still present in the beam.

We see from this table that, although the absorption coefficients of a number of absorbers are in good agreement with each other, the absorption coefficient of certain other elements are markedly different. This difference cannot be ascribed to a normal photoelectric effect because it varies irregularly with atomic number, so that it appears that there is an additional absorbing

Table V.—Table of Results.

Element.	Mass per sq. cm. gm.	Density.	Number of electrons per gm.	Z.	Error.	Experimental value of μ_e.	Filter correction.	Final corrected value μ_e.	τ_e.	$\mu_e - \tau_e$.
					per cent.		per cent.			
Carbon	7·46	1·88	3·03	6	2	127·8	3·2	124·4	0·0	124·4
Sodium	14·66	0·969	2·898	11	1·3	127·6	2·8	125·3	0·0	125·3
Magnesium	9·05	1·740	2·990	12	1·5	128·7	3·05	126·0	0·0	126·0
Aluminium	10·16	2·694	2·992	13	0·75	140·4	2·6	138·1	0·0	138·1
Aluminium	20·64	2·684	2·992	13	0·85	140·9	2·15	139·2	0·0	139·2
Phosphorus	13·6	—	2·931	15	3·4	140·1	2·4	138·1	0·1	138·0
Sulphur	8·89	1·923	3·0244	16	1·3	123·2	3·3	120·3	0·1	120·2
Iron	19·70	7·848	2·822	26	1·3	131·2	2·6	129·0	0·4	128·6
Copper	13·91	8·885	2·765	29	0·7	140·3	2·4	138·3	0·6	137·7
Zinc	17·32	7·10	2·781	30	2·1	126·6	2·9	124·2	0·6	123·6
Cadmium	10·83	8·504	2·587	48	1·7	149·4	3·05	146·3	2·6	143·7
Tin	16·63	7·28	2·553	50	1·45	151·9	2·7	149·3	2·9	146·4
Antimony	10·14	6·662	2·538	51	1·5	140·5	3·4	137·1	3·2	133·9
Pure lead	16·77	11·31	2·398	82	1·0	169·7	3·6	165·2	13·2	152·0
Impure lead	11·45	10·88	2·398	82	1·6	165·7	3·9	160·7	13·2	147·5
Bismuth	9·82	9·768	2·407	83	1·1	165·3	4·6	159·3	13·6	145·7
Wax	12·20	0·9018	3·477	—	0·95	126·4	2·65	124·4	0·0	124·4
Hydrogen (calculated from wax)	—	—	—	—	7·0	—	—	126	0·0	126

mechanism in a number of elements. This irregular variation with atomic number suggests that the additional absorption may be nuclear in origin.

The method of the experiment was designed to preclude spurious abnormalities and in many instances normal and abnormal elements, such as aluminium and magnesium, were bracketed together in the measurements. The value found for aluminium was repeated with another specimen twice as thick, but the same value was obtained. As a control experiment a few measurements were made with the radium (B + C) γ-rays with the following results :—

Table VI.

Element :	Magnesium.	Aluminium.	Lead.	Bismuth.
$\mu_e \times 10^{-27}$	172·7	169·1	227·9	225·0
Error (per cent.)	0·9	1·0	2·0	2·0

The correction for the difference in the reduction of intensity in the magnesium and the aluminium absorbers is more important with the radium than with the thorium rays, because the absorption coefficient is varying more rapidly with filter thickness. This correction accounts for most of the observed difference between the elements magnesium and aluminium, and the elements lead and bismuth, so that the extra absorption is not present for these rays. It is of interest to observe that these figures agreed with those found by other workers using 2·5 cm. filter thickness, so that for radium γ-rays a filter thickness of 3·2 cm. placed immediately in front of the ionisation chamber is equivalent to a 2·5 cm. filter in the more usual disposition.

The experimental values of the absorption coefficients in different elements presented in Table V include an amount of photoelectric absorption which presumably varies from atom to atom as the fourth power of the atomic number. The extent of this absorption is a matter of some considerable uncertainty, and no satisfactory theoretical formula has as yet been given. But it appears probable that the photoelectric absorption per electron for this hard γ-ray ($2 \cdot 649 \times 10^6$ volts) for lead is within 30 per cent. of $13 \cdot 2 \times 10^{-27}$. The values of τ_e for each element were calculated from this and are given in Table V together with the difference between the experimental and the photoelectric absorption.

The photoelectric effect does not account for all of the observed difference between lead and the lighter elements, so that the extra absorption must be present in lead, bismuth, and antimony as well as in the lighter elements tin, copper, cadmium, phosphorus, and aluminium. It is to be emphasised that it is quite certain that the elements tin, cadmium, copper, phosphorus, and aluminium show an additional absorption irrespective of any error in the above estimate of the photoelectric effect, because this experiment itself furnishes an upper limit to the photoelectric absorption in lead of $\tau_e = 40 \cdot 8 \times 10^{-27}$—the difference between the experimental absorptions in lead and in the absorbers carbon, sodium, magnesium, sulphur, iron, zinc and wax.

The mean value of σ_e for the elements which do not show the extra absorption is $124 \cdot 6 \times 10^{-27}$ and has a total error of 1·3 per cent. If a slight extra absorption is present in iron the mean value would be reduced to $124 \cdot 0 \times 10^{-27}$. The corresponding values of σ_e calculated for this ray ($2 \cdot 649 \times 10^6$ volts) on the various theoretical formulæ are as follows :—

Table VII.

Formula.	Compton.	Dirac.	Klein and Nishina.
$\sigma_e \times 10^{-27}$	58·1	70·60	123·5

Thus the experimental value of σ_e for this monochromatic γ-ray is in excellent agreement with the Klein and Nishina formula. The agreement is less satisfactory if the spectroscopic value of e/m be employed, for the theoretical value is then $122 \cdot 7 \times 10^{-27}$. Fortunately, since the elements from which this mean is derived are of low atomic number, this agreement is almost independent of the value of the photoelectric effect employed.

[*Note added in proof.*—Measurements in progress with a steel ionization chamber containing oxygen at 80 atmospheres pressure appear to give a uniform variation of absorption coefficient with atomic number, so that little stress can be laid on the irregularities found in this paper until they have been the subject of a more detailed investigation. These measurements agree with those described in this paper in giving a good agreement with the Klein and Nishina formula for the lighter elements, and in proving that, for the heavy elements, there is present an additional absorption which does not vary with atomic number in the usual manner of the photoelectric effect.]

Summary.

Absorption measurements have been made with thorium C″ γ-rays in a manner which has made it possible to draw unambiguous conclusions concerning the absorption of the hard monochromatic ray having a quantum energy $2 \cdot 649 \times 10^6$ volts.

After applying a correction of 1 per cent. for scattering and about 3 per cent. for the soft component not eliminated by the lead filter, the observed absorption coefficients for certain elements showed that the scattering formula proposed by Klein and Nishina is much more accurate than any hitherto proposed.

Although the absorption coefficients of a number of elements agreed with each other and with the Klein and Nishina formula, yet certain other elements showed an additional absorption which varied irregularly with atomic number and which is presumably nuclear in origin.

I wish to express my appreciation for the interest that Sir Ernest Rutherford has taken in this work, and to thank Dr. Chadwick and Mr. L. H. Gray for their helpful discussion and advice. The work was made possible by a grant from the Department of Scientific and Industrial Research, which I desire to thank.

A Note on the Supposed Dehydration of Hydrated Platin-Cyanides on Cooling.

By Henry Terrey, University College, London.

(Communicated by F. G. Donnan, F.R.S.—Received April 11, 1930.)

In the 'Proceedings of the Royal Society' for 1909,* Prof. J. Emerson Reynolds describes some results on the cooling of hydrated platin-cyanides in liquid air. From a solution of a salt of ascribed formula $Li_2Pt(CN)_5 . 2H_2O$ saturated at 40° C. and then quickly cooled to 15° C., a colourless needle-like crystalline solid exhibiting a slight fluorescence was obtained. This colourless salt was found to contain three molecules of water. By heating or cooling this trihydrate a molecule of water was said to have been lost, giving rise to the red dihydrate, *i.e.*,

$$Li_2Pt(CN)_5\,3H_2O \underset{\text{cooling}}{\overset{\text{heating}}{\rightleftarrows}} Li_2Pt(CN)_5\,2H_2O + H_2O.$$

This example of the loss of water on cooling, although not impossible from phase rule considerations, is the only one known to the author. Observations by Dr. C. H. Stubbs on other coloured hydrated salts did not indicate any such change on cooling.

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* A, vol. 82, p. 380.

Through the kindness of the late Prof. Reynolds a specimen of the trihydrate exhibiting the phenomenon was given to the author. The crystals were sealed in a flask in a moist state. To bring about the change it was found to be unnecessary to employ so low a temperature as that obtained by the use of liquid air. At about − 14° C. the crystals assumed a distinct red colour, the colour disappearing when the temperature was allowed to rise. A red colour was obtained when the crystals were warmed over the flame. Close examination of the cooled crystals showed, however, that they were covered with a slight overgrowth.

Spectroscopic investigation of the Reynolds salt indicated the presence of potassium, and a complete analysis revealed the fact that Reynolds was not dealing with a platinocyanide of the formula $Li_2Pt(CN)_5 . 2H_2O$ but probably with potassium lithium platinocyanide* $KLiPt(CN)_4 . 2H_2O$. On rapidly cooling down a saturated solution of this salt from 40° C. to 15° C. the trihydrate of the potassium salt separates out ($K_2Pt(CN)_4 . 3H_2O$). The platinocyanides have the tendency to absorb on the surface mother liquor and each crystal of the potassium salt is covered with a solution of double salt or double salt and lithium salt. On cooling down to the cryohydric point double salt and ice separate as a film. The double salt dihydrate is of a bright red colour† and the supposed change of the trihydrate to the dihydrate is in reality merely the separation on the surface of each crystal of a film of the coloured cryohydrate.

The reverse change on heating is due to evaporation of the solvent water and the deposition of the red double salt.

Analysis of Reynolds' compound.

Analysis gives :—

Pt, 52·2 ; K, 9·2 ; Li, 2·0 ; CN, 27·6 ; H_2O, 7·7 per cent.

$KLiPt(CN)_4 . 2H_2O$ requires :—

Pt, 51·18 ; K, 10·24 ; Li, 1·82 ; CN, 27·27 ; H_2O, 9·51 per cent.

The experimentally determined values are sufficiently near to indicate that Reynolds was dealing with this double salt.

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* *Cf.* in this connection Martius Inaugural Dissertation, Göttingen, 1850.

† *Cf.* Jolly and Terrey, ' J. Chem. Soc.,' p. 2217 (1923).

The Scattering of Hard Gamma Rays.—Part I.

By L. H. Gray, B.A., Coutts Trotter Student of Trinity College, Cambridge.

(Communicated by Sir Ernest Rutherford, P.R.S.—Received May 5, 1930.)

OUTLINE OF THE PRESENT POSITION.

§ 1. *Summary of Previous Work.*

As early as 1904 it was shown by Eve that the passage of γ-rays through matter was accompanied by the emission of secondary rays somewhat less penetrating than the primary radiation. Experiments by Kleeman, Madsen and Florance led to the conclusion that the secondary radiation was not a fluorescent radiation but a scattered radiation since its quality appeared to be independent of the nature of the radiator. These early investigations prepared the way for an admirable series of experiments by J. A. Gray* which established the main features of the scattering process, showing in particular that the smaller penetrating power of the scattered radiation is due to a change in quality accompanying the act of scattering. As is well-known, a simple quantum explanation of the phenomenon has been given by Compton,† the smaller penetrating power of the scattered radiation being ascribed to the smaller momentum, and therefore longer wave-lengths of the deflected quanta. Recent developments of the quantum theory‡ leave unchanged Compton's relation between the change in wave-length and angle of scattering, since this relation involves only the assumption of the conservation of energy and momentum during the interaction of a quantum and a free electron.

Experimental research since 1913 has in the main been directed towards establishing the angular distribution of intensity of the scattered radiation, and the variation with wave-length of the probability of interaction between a quantum and an electron. The experimental results lend strong support¶ to the theoretical formulæ recently proposed by Klein and Nishina (*loc. cit.*), in fact it now appears probable that over the whole range of wave-lengths investigated, the new quantum mechanics leads to an accurate description of the interaction between a quantum and a free electron. From the standpoint of the older quantum theory all electrons could be regarded as "free" since the binding energy of even the K electrons in lead could be neglected in comparison with the energy of the quantum, which for the γ-rays usually investigated was between 1 and 2 million volts. The scattering power per electron (the scattering coefficient divided by the number of electrons per unit volume) of all substances should therefore be the same. The early measurements of J. A. Gray referred to above showed that this was roughly true of carbon, iron and lead over a limited angular range.

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* 'Phil. Mag.,' vol. 26, p. 611 (1913).

† 'Phys. Rev.,' vol. 21, p. 483 (1923).

‡ Klein and Nishina, 'Z. Physik,' vol. 52, p. 853 (1929).

¶ For a brief discussion of the evidence see Gray, 'Roy. Soc. Proc.,' A, vol. 122, p. 647 (1928), Skobelzyn, 'Nature,' vol. 123, p. 411 (1929), and 'Z. Physik,' vol. 58, p. 595 (1929); Tarrant, *supra*, p. 345.

This conclusion was confirmed for light elements, with varying degrees of accuracy, by the subsequent measurements of Florance, Ishino and A. H. Compton. In each case the scattering power of tin and lead, per electron, appeared to be rather smaller than that of the light elements, but no significance was attached to this result since it might reasonably have been due to an error in correcting for the reabsorption of the scattered radiation.

Owing no doubt, on the one hand, to the strong theoretical grounds for the assumption that each electron scatters equally and independently, and, on the other hand, to the difficulty of the experimental measurement, no accurate and systematic investigation has ever been undertaken of the relative scattering power of different elements.

Two systematic investigations have been made of the total absorption coefficient per electron, which includes the energy removed from the primary beam as recoil electrons as well as the energy of the scattered quanta. Kohlrausch* using hard radium C γ-rays found that for the 20 elements investigated between carbon and molybdenum, the coefficient was constant within the limits of experimental error, though the accuracy of measurement was in some cases only about 5 per cent. Ahmad† confirmed this result for certain light elements with an accuracy of 1 or 2 per cent. using a γ-ray beam of much smaller average quantum energy. Neither of these investigations, however, yields any definite information about the scattering power of heavy elements, since the absorption coefficient then includes a third term of unknown magnitude referring to photoelectric absorption.

The experimental results presented by Tarrant in the previous paper show that the absorption coefficient per electron of the hard thorium C″ γ-rays varies irregularly from element to element in the periodic system, a result which was thus quite unexpected both from the theoretical and the experimental standpoint.

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* 'Wien. Akad. Ber.,' vol. 126, p. 887 (1917).

† 'Roy. Soc. Proc.,' A, vol. 105, p. 507 (1924).

§ 2. *The Significance of the New Measurements.*

Since the absorption coefficient of the hard thorium C″ γ-rays in a number of light elements has been found to be in good agreement with the theoretical Klein-Nishina values, while in other elements, the experimental value exceeds the theoretical, the conclusion has been drawn, tentatively, that a new absorbing mechanism is operative in these elements, and reasons have been adduced for associating the mechanism with the nuclei of the abnormal elements. Without, however, prejudicing the issue with regard to the origin of the additional absorption, the question naturally arises as to the extent to which the abnormally large absorption coefficients are due to an increase in the true absorption or in the deflection of γ-ray energy.

A direct method of investigation would be to compare the intensity of the radiation scattered by a pair of elements such as sulphur and aluminium, one of which behaves according to theory, the other showing an additional absorption. Unfortunately such a comparison is difficult to carry out in practice using the hard thorium C″ γ-rays on account of the weakness of the available source. Much larger radium (B + C) sources are available, and by filtering through 4 cm. of lead a γ-ray beam is obtained consisting of quanta of mean energy somewhat greater than $1\frac{1}{2}$ million volts. The energy is spread over a wide range of wave-lengths and includes a small proportion which is comparable in hardness with the thorium C″ γ-radiation. It seemed worth while, therefore, as a preliminary investigation, to carry out a comparison of the scattering power of aluminium, sulphur and lead for hard radium C γ-rays.

Owing to large corrections for reabsorption the measurements made with lead were not very accurate. The aluminium-sulphur comparison, however, is probably reliable to 0·5 per cent. and with regard to the energy scattered between 16° and 90° showed no certain difference in the scattering power, per extra-nuclear electron, of the two elements. A new high pressure ionisation chamber has been constructed with which it is hoped to repeat the comparison using the hard thorium C″ γ-rays.

The significance of the negative result obtained with hard radium C γ-rays is discussed in § 9. It appears, either that no considerable proportion of the energy absorbed in the new way is re-emitted in the forward direction between 16° and 90°, or that the new absorbing mechanism is almost entirely inoperative in aluminium in the case of quanta of energy $1 \cdot 5 \,.\, 10^6$ ε-volts, and only becomes of considerable magnitude as the quantum energy approaches close to that of the hard thorium C″ line ($2 \cdot 65 . 10^6$ ε-volts).

As an alternative to deflection or re-emission there is the possibility that the γ-ray energy is converted into corpuscular energy, a process which would be expected to manifest itself as an increased ionisation in vessels of which the walls are composed of "abnormal" elements. The ionisation produced by a radium (B + C) γ-ray beam filtered through 4 cm. of lead has been measured by the author using small ionisation chambers composed of carbon, aluminium and sulphur. The ionisation per unit volume in the three chambers was identical to within 1 per cent. which was the order of accuracy of the measurement. It has been shown* that the ionisation in a small chamber depends only on the γ-ray energy absorbed per unit volume, and on the rate of loss of energy by β-particles, in the material of the walls. In the case of a "normal" element the former is proportional to the number of electrons per unit volume, and from the work of J. A. Gray and Sargent† we know that the latter is very approximately inversely proportional to this quantity. Since aluminium has been bracketed by the two normal elements carbon and sulphur it seems probable that the γ-ray energy actually absorbed per electron in aluminium is within 1 per cent. of that absorbed in normal elements.

Since both scattering and absorption measurements with hard radium C γ-rays have failed to distinguish between aluminium and sulphur, the evidence seems to point to the conclusion that the new absorbing mechanism in aluminium does not manifest itself until the energy of the quanta is in the neighbourhood of $2 \cdot 5 . 10^6$ ε-volts.

It is particularly unfortunate that the comparison of the scattering power of aluminium and lead, described below, has not yielded any accurate results, since such a comparison has clearly a great advantage over a direct absorption measurement in which the total scattering coefficient can only be deduced when the magnitude of the photoelectric absorption is known. After making a reasonable allowance for photoelectric absorption, Tarrant's experimental results lead to an estimate of the residual absorption of the hard thorium C″ γ-rays in the lead considerably greater than that in sulphur (the additional absorption in lead is about twice that in aluminium). There is also evidence of an additional absorption in lead in the case of radium C γ-rays which have been filtered through at least 4 cm. of lead. It is hoped that with the new ionisation chamber, and a slightly modified canalising system it may be possible to determine the scattering power of lead with sufficient accuracy to throw light on these conclusions.

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* L. H. Gray, *loc. cit.*

† Gray and Sargent, 'Trans. Roy. Soc. Can.,' vol. 21, p. 173 (1927); Sargent, *ibid.*, vol. 22, p. 179 (1928).

DETAILED ACCOUNT OF THE SCATTERING EXPERIMENT.

The result of the measurement of the relative scattering power of sulphur and aluminium for hard radium γ-rays has already been presented, but in these, as in other γ-ray measurements, it is desirable to record in some detail the exact disposition of apparatus and experimental procedure.

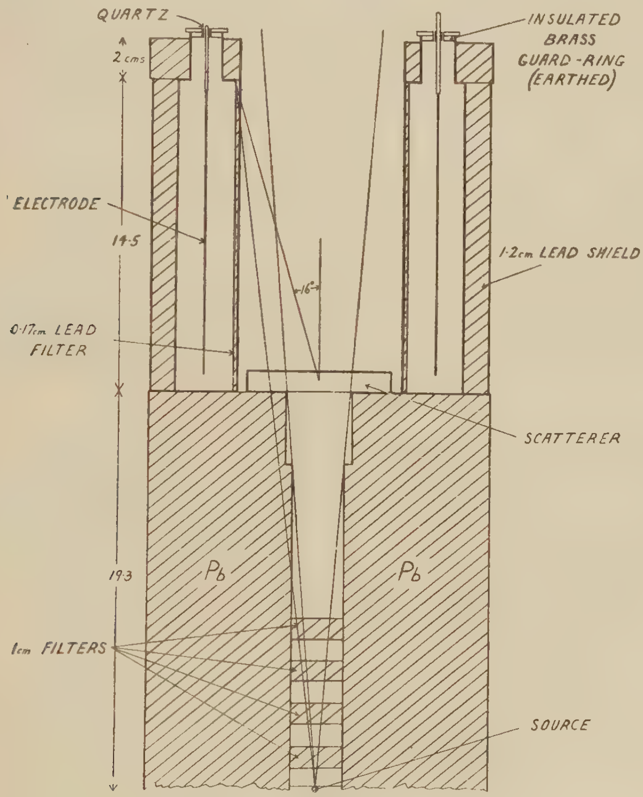
QUARTZ
INSULATED BRASS GUARD-RING (EARTHED)
2 cms
ELECTRODE
14·5
1·2cm LEAD SHIELD
16°
0·17cm LEAD FILTER
SCATTERER
Pb
Pb
19·3
1cm FILTERS
SOURCE

FIG. 1.

§ 3. *General Principles Embodied in the Experimental Disposition.*

A small glass bulb containing radon having initially an activity equivalent to 160 mgm. of radium, was situated, as shown in the figure, near the base of a set of cylindrical lead canalising blocks, about 20 cm. high. The source was left undisturbed throughout the measurements. The filter consisted of four lead discs, each 1 cm. thick. These were spaced 1 cm. apart, since it has been shown by J. A. Gray that such an arrangement produces a greater hardening than when the filter consists of a single disc of the same total thickness.

By filling the remainder of the central hole with a lead plug it was found that the direct radiation from the source after passing through the canalising blocks produced an ionisation of about 420 J (ions per cubic centimetre per second) in the annular chamber.

The apparatus was mounted on a light wooden stand, and was set up at least a metre from any other object. In this way it was secured that once scattered radiation from surrounding objects will consist of quanta deflected through at least 160°, and consequently having a wave-length of at least 46 X.U. and an absorption coefficient in lead greater than 5 cm.^{-1}. By surrounding the chamber with $1 \cdot 2$ cm. lead it was thus possible to reduce the stray scattered radiation to less than $0 \cdot 003$ of its initial intensity. Without this shield the ionisation due to the stray radiation was found to be 750 ions per cubic centimetre per second.

The hard radiation passing through the filters was unfortunately contaminated by a small proportion of softer radiation scattered from the inner walls of the canalising blocks. This point will subsequently be discussed more fully.

The electron content per unit area of the sulphur and aluminium scatterers only differed by 2 per cent. In comparing the scattering power of these two elements, therefore, the corrections to be applied for the partial absorption of the direct radiation and of the radiation scattered from the canal walls, and the partial reabsorption of the scattered radiation under investigation were nearly identical for the two elements.

Owing to photoelectric absorption, these corrections were much greater in lead than in aluminium, and introduced a correspondingly large uncertainty into the comparison of the scattering powers.

§ 4. *The Ionisation Chamber.*

A sealed ionisation chamber was used, filled with air at atmospheric pressure, and having a natural activity of 20 ions per cubic centimetre per second. This small natural activity is to be attributed to the fact that the chamber was constructed in a workshop into which radioactive material had never been introduced.* The chamber was annular in form and made of brass 2 mm. thick. The collecting electrode, consisting of a cylindrical piece of zinc gauze, was insulated from the earthed brass plugs by quartz tubing set in sealing-wax. The brass plugs were insulated by sealing wax from the case, which was raised to a potential of 40 volts. The electrode system was connected to the electrometer by a wire passing through evacuated earthed tubes. By reversing the potential on the chamber that part of the total current due to ionisation in the chamber itself could be deduced. The ionisation in the remainder of the apparatus was less than 2 per cent. of the whole.

Before reaching the chamber the radiation from the scatterer passed through a cylindrical sheet of lead 0·17 cm. thick. This was introduced with the object of absorbing the fluorescent radiation from the lead scatterer, but was present throughout the measurements. The ionisation currents were measured by the Townsend balance method, using a Compton electrometer at a sensitivity of about 2,500 divisions per volt. The total observed current comprised the following contributions.

Direction radiation	420 J
Stray scattered radiation	2 J
Radiation scattered from canal walls	217 J
Natural activity of chamber	20 J
Total	659 J
Increase in ionisation on introducing scatterer	127 J
Ionisation due to scattered radiation, after allowing for re-absorption, etc.	193 J

§ 5. *Experimental Procedure.*

Measurements were made alternately with the aluminium and sulphur scatterers in position as indicated in Table I. The currents are measured in ions per second, about $1 \cdot 5 \times 10^9$ ions being collected in the measurement of any one current. If the whole of the natural activity of the chamber is attributed to α-particle ionisation, the calculated probable error of each current is about 0·1 per cent. The observed fluctuations were somewhat less than half this amount.

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* I am greatly indebted to Mr. T. E. Harris of Denver, Norfolk, for constructing the chamber in his private workshop, and to Prof. C. T. R. Wilson for allowing me to reassemble it at the Cambridge Observatory.

Table I.—Strength of source = 160 mgm. equivalent activity. Volume of ionisation chamber = 1400 c.c.

Date	Time.	Experiment.	Ionisation Current in ions per second.	Current minus natural activity.	Current corrected for decay of source.
Nov. 19, '29	1.34	Aluminium	10·977 . 10^5	10·674 . 10^5	10·965
	2.32	Sulphur	10·938	10·635	11·005
	3.28	Aluminium	10·836	10·533	10·976
	4.27	Sulphur	10·801	10·498	11·022
	5.24	Aluminium	10·707	10·404	11·000
	5.57	No scatterer	8·985	8·682	9·218
Nov. 20, '29	10.18	Sulphur	9·506	9·203	11·054
	11.18	Aluminium	9·378	9·075	10·984
	12.19	Sulphur	9·335	9·032	11·016
	1.43	Aluminium	9·235	8·932	11·010
	2.50	Sulphur	9·180	8·877	11·035
	3.54	Aluminium	9·099	8·796	11·022
	4.55	Sulphur	9·057	8·754	11·054
Nov. 21, '29	11.48	Aluminium	7·338	7·035	10·244
	1.01	Lead	7·040	6·737	9·898
	2.12	Aluminium	7·192	6·889	10·214
	3.44	Lead	6·885	6·582	9·872
	4.58	Aluminium	7·030	6·727	10·184
Nov. 22, '29	12.14	No scatterer	5·570	5·267	9·222
	3.51	No scatterer	5·422	5·119	9·210
	5.25	Central hole filled by lead plug	3·692	3·389	6·169
Nov. 23, '29	12.22	Chamber unshielded from stray radiation	8·758	8·455	17·76
Nov. 30, '29	9.0–1.0	Natural activity	0·303	0·303	0·303

The observed ionisation currents, after correcting for the decay of the source, are shown graphically in fig. 2. No explanation has been found for the slight gradient of the lines. Inasmuch as it is positive on two occasions and negative on the third it can hardly be due to a decreasing natural activity such as might arise through the fact that it was found necessary to open and reseal the ionisation chamber 5 days before the measurements were commenced.

§ 6. *Dimensions of Scatterers.*

The scatterers were in the form of discs of about 5 cm. radius. Since the radius of cross section of the γ-ray beam at the scatterer was 1·53 cm., only the central portion of the scatterer was effective. The contours of the scatterer were determined accurately in each case with a micrometer screw gauge, from which the mean density of the whole, and the mean thickness of the

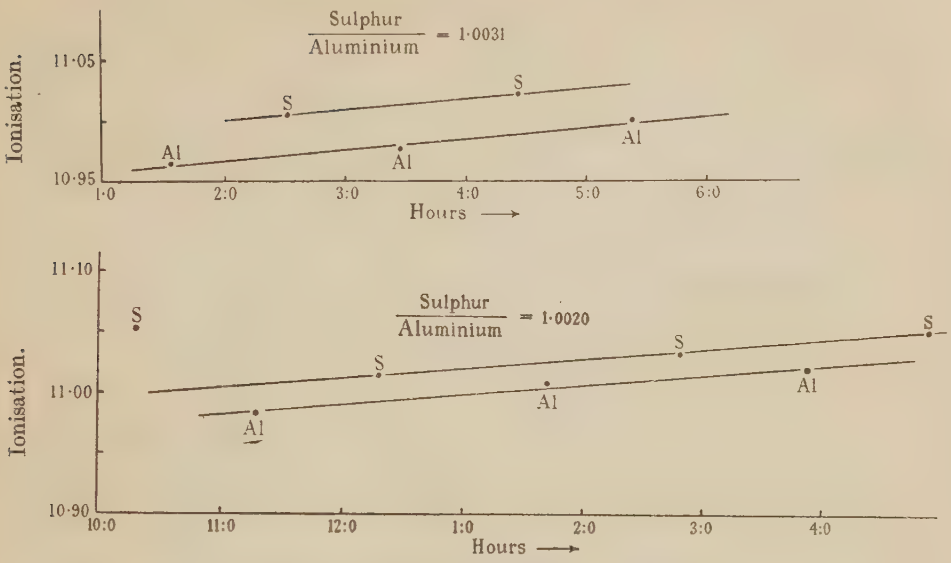

FIG. 2A.—Scattering by Aluminium and Sulphur.

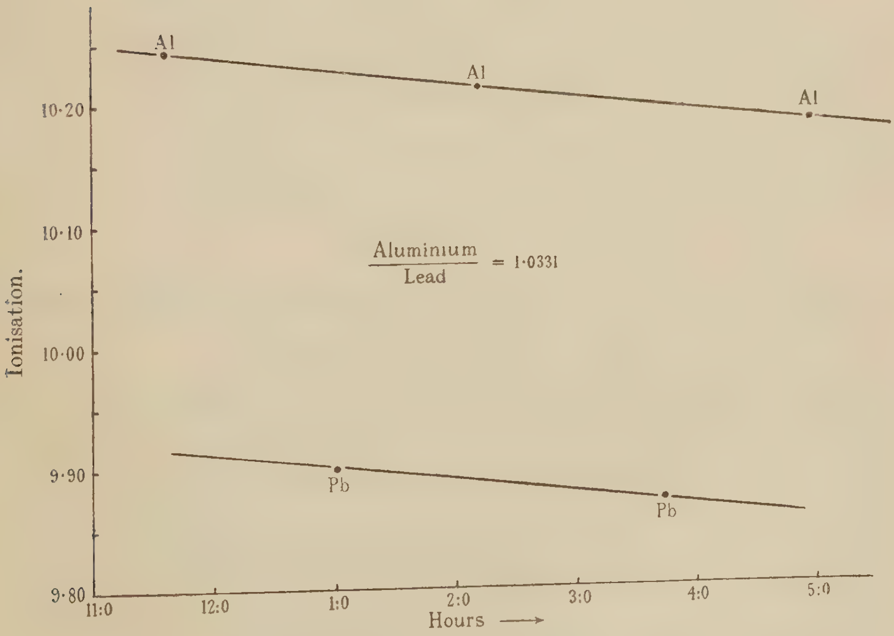

FIG. 2B.—Scattering by Aluminium and Lead.

portion traversed by γ-rays could be determined. The figures given for the superficial electron density should certainly be accurate to 0·1 per cent.

Table II.

	Aluminium.	Sulphur.	Lead.
Mean density	$2 \cdot 706$ gms./cm.^{3}	$1 \cdot 940$ gms./cm.^{3}	$11 \cdot 32$ gms./cm.^{3}
Effective thickness, No. I	$0 \cdot 5356$ cms.	$0 \cdot 6325$ cms.	$0 \cdot 1623$ cms.
,, No. II	$0 \cdot 5637$ cms.	$0 \cdot 8749$ cms.	—
,, I + II	$1 \cdot 0993$ cms.	$1 \cdot 5074$ cms.	—

$$\frac{\text{Electron density of sulphur (I + II)}}{\text{Electron density of aluminium (I + II)}} = \frac{1 \cdot 5074 \,.\, 1 \cdot 940 \,.\, 13 \,.\, 32 \cdot 06}{1 \cdot 0993 \,.\, 2 \cdot 706 \,.\, 16 \,.\, 26 \cdot 96} = 1 \cdot 0198.$$

$$\frac{\text{Electron density of aluminium (I)}}{\text{Electron density of lead (I)}} = \frac{0 \cdot 5356 \,.\, 2 \cdot 706 \,.\, 16 \,.\, 207 \cdot 2}{0 \cdot 1623 \,.\, 11 \cdot 32 \,.\, 82 \,.\, 26 \cdot 96} = 0 \cdot 9612.$$

§ 7. *Calculation of Relative Scattering Power of Sulphur and Aluminium.*

The mean value of the ratio of the total ionisation with the sulphur scatterer in position, to that when the aluminium scatterer is in position, as deduced from the experimental curves of fig. 2A is

$$I_s / I_{al} = 1 \cdot 0025. \tag{1}$$

Denoting the increase in ionisation on introducing the aluminium and sulphur scatterers by A and S respectively, and adopting the mean value*

$$A = 1 \cdot 784$$

the above ratio (1) leads to

$$S = 1 \cdot 811.$$

In order to deduce the relative scattering power of the two elements a number of corrections must be applied.

(*a*) *Correction for Absorption by the Scatterer of Radiation Scattered from the Canal Walls.*—This correction is difficult to apply because neither the angular distribution nor the wave-length of the scattered radiation are accurately known. However, if we make the assumption that these are the same as from the scatterer itself, then we may make the correction with sufficient accuracy with the help of the curves of fig. 3 and other similar curves.

Curve I shows the distribution of scattered energy for the mean wave-length of the primary beam ($7 \cdot 0$ X.U.) and curve II the ionisation produced by this radiation after passing through the $0 \cdot 17$ cm. lead filter on the inside of the chamber.

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* The unit of current adopted for the purpose of these calculations is 10^5 ions per second.

Curve III shows the extent to which this ionisation is reduced by the absorption of the scattered radiation in the two aluminium scatterers (I + II),

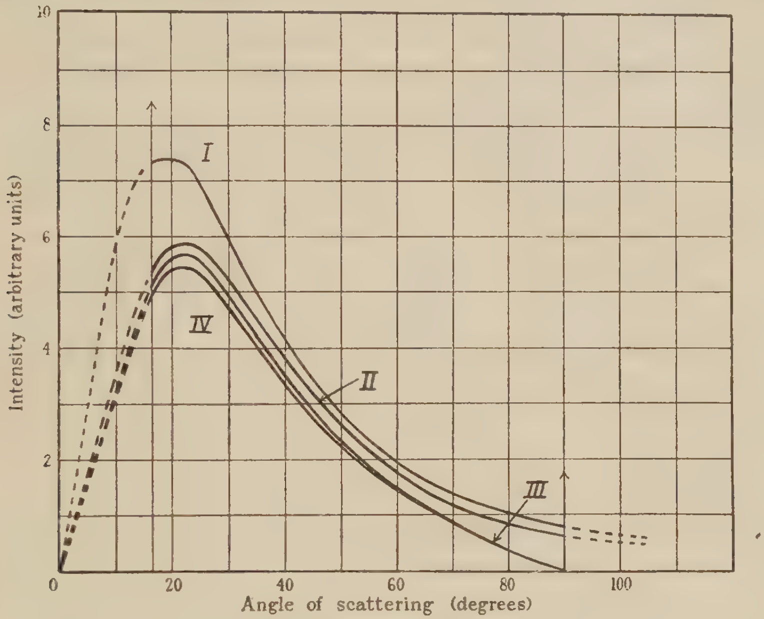

FIG. 3.

and curve IV the result of absorption in the lead scatterer. In calculating these curves it was found that the appropriate absorption coefficients to use were :—

$$\sigma_a + 0\cdot15\,\sigma_s$$

for absorption in aluminium, and

$$\sigma_a + 0\cdot15\,\sigma_s + \tau$$

for absorption in lead, where σ_a, σ_s and τ are absorption coefficients referring to the recoil electrons, the scattered quanta, and photoelectric absorption respectively, since all but about 15 per cent. of the scattered energy passes through the chamber.

In this way we find that by absorbing the canal rays, the introduction of the scatterers causes a reduction in ionisation of amount :—

Aluminium $0\cdot442$ Sulphur $0\cdot450$.

Adding these to the figures given above for the observed increase in ionisation on introducing the scatterers, we have :—

$$A' = 2\cdot226 \qquad S' = 2\cdot261.$$

These figures do not represent the whole of ionisation due to the scattered radiation since this radiation is partly reabsorbed in the scatterer.

(*b*) *Correction for Reabsorption in Scatterer.*—Using curves similar to those shown in fig. 3 and assuming that the absorption is the same as if all the scattered radiation were generated at the centre of the scatterer, we find for the reabsorption

Aluminium 8·41 per cent. Sulphur 8·58 per cent.

Allowing for reabsorption we therefore have

$$A'' = \frac{2\cdot226}{91\cdot59} = 2\cdot430, \qquad S'' = \frac{2\cdot261}{91\cdot42} = 2\cdot473.$$

Two further small corrections are necessary.

(*c*) Since the superficial electron density in the sulphur scatterer was greater than in the aluminium, the primary beam will be slightly more absorbed in the former case.

(*d*) Owing to the much smaller density and therefore greater thickness of the sulphur scatterer, the centre of the scatterer is nearer to the top of the chamber and the radiation passing through the chamber is that scattered within slightly smaller angular limits than in the case of aluminium.

The two corrections (*c*) and (*d*) are in the same sense and together amount to 0·46 per cent. Increasing S″ by this amount, we have finally

$$A_0 = 2\cdot430 \qquad S_0 = 2\cdot484$$

and their ratio gives the relative amount of energy scattered by the two specimens, viz.,

$$S_0/A_0 = 1\cdot0223.$$

Since the ratio of the superficial electron densities was found above to be 1·0198, we arrive at the relative scattering power per electron :

$$\text{Sulphur/Aluminium} = 1\cdot002_5.$$

It will be observed that this value of the ratio, after applying all four corrections, differs from the apparent ratio, derived directly from experiment by about 0·7 per cent. It is unlikely that the application of these corrections introduces an uncertainty as great as 0·2 per cent.

Allowing as experimental error, the difference from the mean of the ratio determined from either of the two sets of curves of fig. 2, viz., 0·2 per cent., and allowing also 0·1 per cent. uncertainty in the measurement of the dimensions of the scatterers, the probable error is less than 0·5 per cent.

The scattering per extra-nuclear electron is therefore the same in aluminium and sulphur within the limits of experimental error, as judged by measurements of the radiation scattered between 16° and 90° under the conditions indicated in fig. 1.

Thus, in marked contrast with Tarrant's thorium C″ γ-ray absorption measurements, these experiments indicate that it is unlikely that the scattering of hard radium C γ-rays by aluminium exceeds that by sulphur by as much as 0·25 per cent.

§ 8. *The Relative Scattering Power of Aluminium and Lead.*

The experimental data referring to aluminium and lead have been treated in a manner precisely similar to that outlined above.

From fig. 2 we deduce the following values for the increase in ionisation on introducing the scatterers :—

$$\mathrm{Al} = 0{\cdot}995 \qquad \mathrm{Pb} = 0{\cdot}668.$$

Correcting for the absorption of canal rays, and the re-absorption of scattered radiation, these figures become

$$\mathrm{A}'' = 1{\cdot}307 \qquad \mathrm{P}'' = 1{\cdot}220.$$

Applying also corrections (*c*) and (*d*) above, we find

$$\mathrm{P}_0/\mathrm{A}_0 = 0{\cdot}947.$$

Dividing by the relative electron densities, the scattering power of lead, per electron, is found to be only 91 per cent. of that of aluminium.

Owing to the magnitude of the corrections which have been applied, this difference cannot be regarded as significant.

§ 9. *Discussion of the Aluminium-Sulphur Comparison.*

If the anomalous absorption found by Tarrant is not a resonance phenomenon, then the fact that no evidence of a similar effect has been found in any experiments concerned with the absorption of the radium C γ-rays in aluminium makes it probable that the new absorbing mechanism in aluminium is only effective for very hard quanta. This leads us to form an estimate of the spectral distribution of energy in the beam under investigation in the scattering experiments which have just been described.

The approximate spectral distribution of energy in a beam of γ-rays from radium (B + C) after filtering through 4 cms. of lead is shown in fig. 4. This distribution is calculated from the experimental data of Skobelzyn.* In allowing for the hardening effect of the filter an unpublished empirical formula for the variation of the photoelectric coefficient with wave-length has been used which is certainly much more in accordance with observation than the λ^3 law and is sufficiently accurate for the present purpose.

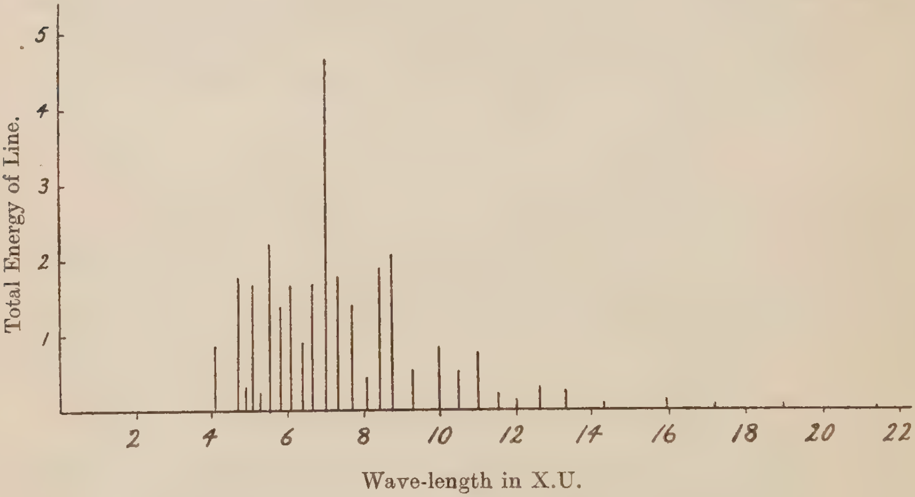

Fig. 4.—Radium (B + C) Gamma Rays, 4 cm. Lead Filter.

Suppose for simplicity that the new absorbing mechanism became fully operative for all quanta having an energy greater than a certain threshold value. We shall refer to the two portions of the beam on either side of the threshold as the "hard" and the "soft" rays. If the threshold is set at one and a half million volts, then 72 per cent. of the energy in the main beam will consist of hard quanta. However, the main beam was contaminated with radiation scattered from the canal walls. From the circumstances that the ionisation produced by these "canal rays" was about equal to that due to the scattered radiation under investigation, we can calculate the relative intensities of the canal rays and the main beam. Since we are investigating the scattered energy, the quantity with which we are concerned is the energy of the beam multiplied by the mean scattering coefficient. A rough calculation leads to the following proportions :—

Hard.	Soft.	Canal (soft).
56	32·5	11·5

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* 'Z. Physik,' vol. 58, p. 595 (1929).

Having regard to the limits of error estimated in § 7 we may conclude that the energy scattered in the forward direction (between 16° and 90°) per electron by aluminium does not exceed that by sulphur by as much as 1 per cent. even when the incident beam consists entirely of quanta of energy greater than $1\frac{1}{2}$ million volts.

If we set the threshold at 4·70 X.U. (the wave-length of the hard thorium C″ γ-rays), then the calculated proportions are :—

Hard.	Soft.	Canal.
4·9	85·9	9·2

Thus, of the measured ionisation only 5 per cent. referred to quanta having initially wave-length equal to or less than 4·7 X.U. Tarrant found the absorption in aluminium to be 15 per cent. greater than that in sulphur. If the additional amount of energy were re-emitted equally in all directions, the observed scattering by aluminium would have been expected to exceed that by sulphur by about 0·4 per cent. The estimated upper limit set by the experiment was only 0·25 per cent., but there are too many uncertainties in the above theoretical considerations to allow any stress to be laid on this discrepancy.

It appears, therefore, either that no considerable portion of the energy absorbed in the new way is re-emitted in the forward direction between 16° and 90°, or that the new absorbing mechanism is almost entirely inoperative in aluminium in the case of quanta of energy $1 \cdot 5 \,.\, 10^6$ ε-volts, and only becomes of considerable magnitude as the quantum energy approaches close to that of the hard thorium C″ line ($2 \cdot 65 \,.\, 10^6$-volts).

I wish to express my thanks to Sir Ernest Rutherford and Dr. J. Chadwick for the interest they have taken in this work, and to Mr. G. R. Crowe for the preparation of the radioactive sources. In preparing the first section of this paper I have been greatly assisted by frequent discussions with Dr. C. D. Ellis and Mr. G. T. P. Tarrant.

The Wake in Fluid Flow Past a Solid.

By Harold Jeffreys, M.A., D.Sc., F.R.S.

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1. A striking feature of modern hydrodynamics is the number of instances where cyclic irrotational motion, with local filaments of vorticity, is used as a valid approximation to the motion of a real fluid. By a real fluid I necessarily mean a viscous fluid. It has been well established, especially in the Kutta-Joukowsky theory of the aerofoil in two dimensions, its generalization to three dimensions by Lanchester and Prandtl, and in Karman's theory of double rows of travelling vortices, that the results are in good quantitative agreement with experiment, accounting for the forces on an immersed solid in all directions with respect to the general flow of the current. The existence of cyclic motion is in disagreement with classical hydrodynamics, which predicts that there shall be no circulation about any circuit drawn in a fluid initially at rest or in uniform motion, and that there is no resultant thrust on a solid immersed in a steady uniform current.

Considerable attention has been given to the reason why classical hydrodynamics fails to represent the experimental facts ; but it appears to me that these efforts arise from an incorrect point of view. The classical fluid differs from the real fluid in two fundamental respects. It can slip freely over a solid boundary without resistance ; the actual fluid has no velocity relative to any solid surface in contact with it. In the classical fluid, the stress across any small surface element within the fluid is exactly perpendicular to that element ; in the real fluid it is, in general, inclined to it. In one respect, the classical fluid is more constrained than the real fluid ; in the other it is less so. In these circumstances, the remarkable thing is not that classical hydrodynamics is often wrong, but that it is ever nearly right. Classical hydrodynamics ceased to be a representation of the physical facts when Poiseuille showed that liquid flowing through a capillary tube was at rest when in contact with the sides of the tube.

In the flow of fluids around solids, the incorrect boundary condition assumed by the classical theory appears to be the dominating cause of the difference between classical flow and actual flow. For let us consider what would happen if we combined the actual condition that there is no relative velocity in any direction where the fluid is in contact with a solid, with the classical result that there is a velocity potential. The motion of any solid can be expressed as a translation of its centroid together with a rotation about it; the components of velocity have the forms

$$u - y\omega_3 + z\omega_2, \quad v - z\omega_1 + x\omega_3, \quad w - x\omega_2 + y\omega_1, \tag{1}$$

in a familiar notation, x, y and z being co-ordinates referred to the centroid. The velocity components of the fluid in contact with the solid are equal to the local values of these expressions. Now consider a volume of fluid within a solid vessel, and containing immersed solids. Take Green's theorem in the form

$$\iint \phi \frac{\partial \phi'}{\partial n} d\mathrm{S} = \iint \phi' \frac{\partial \phi}{\partial n} d\mathrm{S}, \tag{2}$$

where ϕ and ϕ' satisfy Laplace's equation within a region and have no singularities within it, and the surface integrals are taken over the boundaries of the region. The element dn is taken along the normal drawn outward from the fluid. Take ϕ to be the actual velocity potential and ϕ' to be $1/r$, where r is the distance from some point P in the fluid. Take the integrals over all the solid boundaries together with a small sphere described about the point P. Then we have

$$4\pi\phi_{\mathrm{P}} = \iint \frac{1}{r} \frac{\partial \phi}{\partial n} \,.\, d\mathrm{S} - \iint \phi \frac{\partial}{\partial n}\left(\frac{1}{r}\right) d\mathrm{S}. \tag{3}$$

Now if ds is an element of length in the solid boundary, the velocity along it is $\partial\phi/\partial s$, and the difference of the values of ϕ at two points Q and R on the same solid boundary is

$$\int_{\mathrm{Q}}^{\mathrm{R}} \frac{\partial \phi}{\partial s} ds = \int \{(u - y\omega_3 + z\omega_2)\, dx + (v - z\omega_1 + x\omega_3)\, dy + (w - x\omega_2 + y\omega_1)\}\, dz. \tag{4}$$

In order that this may have the same value for all possible paths from Q to R drawn on the boundary, we must have everywhere on the boundary

$$\begin{aligned} l &\left\{\frac{\partial}{\partial z}(v - z\omega_1 + x\omega_3) - \frac{\partial}{\partial y}(w - x\omega_2 + y\omega_1)\right\} \\ &+ m\left\{\frac{\partial}{\partial x}(w - x\omega_2 + y\omega_1) - \frac{\partial}{\partial z}(u - y\omega_3 + z\omega_2)\right\} \\ &+ n\left\{\frac{\partial}{\partial y}(u - y\omega_3 + z\omega_2) - \frac{\partial}{\partial x}(v - z\omega_1 + x\omega_3)\right\} = 0 \end{aligned} \tag{5}$$

by Stokes's theorem, where l, m, n are the direction cosines of the inward normal. This gives at once

$$l\omega_1 + m\omega_2 + n\omega_3 = 0. \tag{6}$$

But the normals at different points can be in any direction, and this can be satisfied only if

$$\omega_1 = \omega_2 = \omega_3 = 0. \tag{7}$$

No solid in contact with a fluid can therefore be rotating.* Its motion is a pure translation, and

$$\Big[\phi\Big]_{\mathrm{Q}}^{\mathrm{R}} = \Big[ux + vy + wz\Big]_{\mathrm{Q}}^{\mathrm{R}}. \tag{8}$$

For any solid we can therefore find a quantity ϕ_0, independent of position, such as that over the boundary

$$\phi = \phi_0 + ux + vy + wz. \tag{9}$$

Then from (3)

$$4\pi\phi_{\mathrm{P}} = \Sigma \iint \frac{1}{r}(lu + mv + nw)\, d\mathrm{S} - \Sigma \iint (\phi_0 + ux + vy + wz) \frac{\partial}{\partial n}\left(\frac{1}{r}\right) d\mathrm{S}, \tag{10}$$

the summations being over all the solids. But the integrands are definite functions of x, y and z, without singularities inside the solids; and

$$lu + mv + nw = \frac{\partial}{\partial n}(\phi_0 + ux + vy + wz). \tag{11}$$

Hence the contribution from the immersed solids is

$$\Sigma \iiint \left\{\frac{1}{r}\nabla^2(\phi_0 + ux + vy + wz) - (\phi_0 + ux + vy + wz)\nabla^2\left(\frac{1}{r}\right)\right\} d\tau \tag{12}$$

taken through all the interiors of the immersed solids; and this is zero. For the enclosing vessel, we may consider the region between it and a large sphere with centre P, and infer

$$4\pi\phi_{\mathrm{P}} = \iint \frac{1}{r}(lu + nv + nw)\, d\mathrm{S} - \iint (\phi_0 + ux + vy + wz) \frac{\partial}{\partial r}\left(\frac{1}{r}\right) d\mathrm{S}, \tag{13}$$

where u, v, w, ϕ_0 have the values appropriate to the enclosing vessel, and the integrals are now over the large sphere. The first integral vanishes since u, v, w and r are constants. The second gives

$$\phi_{\mathrm{P}} = \phi_0 + ux_0 + vy_0 + wz_0, \tag{14}$$

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* Exceptional cases may arise if there are restrictions on (l, m, n), as for a plane or a cylinder; but these need not detain us.

where (x_0, y_0, z_0) are the mean values of x, y, z over the large sphere and therefore are the co-ordinates of P with respect to the centroid of the enclosing vessel. It follows that the velocity components at P are (u, v, w), which are constants, and that the only possible motion is one such that the whole of the solids and the containing vessel move with a single velocity of translation; no solid can rotate. A classical fluid is more rigid than any solid.

This bizarre result of trying to combine irrotational flow with the correct boundary conditions has already been stated as probable, but without proof.* To combine the correct boundary conditions with reasonable arbitrariness in the motions of the solids in contact with the fluid, it is necessary to have greater flexibility in the differential equations that hold in the body of the fluid. This is provided by the fact that in the real fluid the stress is no longer exactly normal to the surface-element; this fact introduces into the equations of motion the viscosity terms, which raise the order of the equations by unity and make it possible to satisfy the boundary conditions.

2. In a viscous fluid, the circulation theorem of classical hydrodynamics is replaced by the following more general form,†

$$\frac{d\Omega}{dt} = \int_{\mathrm{C}} \frac{1}{\rho} \left\{ - dp - \tfrac{2}{3} d\,(\mu\delta) + \frac{\partial}{\partial x_k} (\mu \xi_{ik})\, dx_i + 2 \frac{d\mu}{dx_k} du_k + 2\mu\, d\delta \right\}. \qquad (1)$$

Here Ω is the circulation about a contour C moving with the fluid; the Cartesian co-ordinates of position are x_i; the velocity components u_i; and the summation convention is used. Also

$$\delta = \frac{\partial u_i}{\partial x_i}, \qquad (2)$$

$$\xi_{ik} = \frac{\partial u_i}{\partial x_k} - \frac{\partial u_k}{\partial x_i}, \qquad (3)$$

and the other letters have their usual meanings. In a homogeneous fluid, with the density a function of the pressure alone,

$$\frac{d\Omega}{dt} = \int_{\mathrm{C}} \nu \frac{\partial \xi_{ik}}{\partial x_k} dx_i \qquad (4)$$

$$= \int_{\mathrm{C}} \nu \left(\nabla^2 u_i - \frac{\partial \delta}{\partial x_i} \right) dx_i = \int_{\mathrm{C}} \nu \nabla^2 u_i \, dx_i. \qquad (5)$$

It follows that, in the ordinary conditions of flow over solid boundaries, if the circulation is zero around a contour and the vorticity zero on the contour and near it, the circulation around that contour is not changing with the time. Hence circulation cannot arise spontaneously within a fluid; it must be diffused inwards from a boundary. On the other hand, the existence of circulation is implied by the fact that classical hydrodynamics does not satisfy the facts; there must be circulation in contours near solid boundaries, and this must be diffusing into the body of the fluid. It is therefore to be expected that there will be no appreciable circulation except on contours part of which have passed near a solid boundary; in other words, the vorticity is negligible except in the wake.

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* 'Phil. Mag.,' vol. 50, pp. 815–819 (1925).

† 'Proc. Camb. Phil. Soc.,' vol. 24, pp. 477–479 (1928).

We can show by cross-differentiation of the equations of motion that (1) is equivalent to*

$$\frac{d\xi_{12}}{dt} - \xi_{12}\frac{\partial u_3}{\partial x_3} - \xi_{23}\frac{\partial u_1}{\partial x_3} - \xi_{31}\frac{\partial u_2}{\partial x_3} = \nu\nabla^2\xi_{12}. \tag{6}$$

In the important case of two-dimensional motion parallel to the plane of x_3 constant, two of these equations become identities, and the third is

$$\frac{d\xi_{12}}{dt} = \nu\nabla^2\xi_{12}. \tag{7}$$

Thus vorticity is diffused from the boundary according to the equation of conduction of heat. If fluid has been flowing over a boundary for time t, the vorticity contains a factor $e^{-z^2/4\nu t}$, where z is the normal distance from the boundary. At distances large compared with $2(\nu t)^{\frac{1}{2}}$ the motion is practically irrotational on account of the smallness of this factor. This result constitutes the theoretical justification of the "boundary-layer" theory of Prandtl and his followers.

3. Now consider a liquid with a general velocity U impinging on a fixed solid immersed in it. The dimensions of the solid are of order c parallel to the general velocity and d at right angles to it. Then the time taken for an element of the fluid to pass the solid is of order c/U, and the thickness near the solid of the layer with notable vorticity is of order

$$2(\nu c/\mathrm{U})^{\frac{1}{2}} = l, \text{ say.} \tag{1}$$

At any point of the surface take the axis of z normally, and the axis of x in the direction of the resultant tangential stress. From the equation of continuity

$$\frac{\partial w}{\partial z} = -\frac{\partial u}{\partial x} - \frac{\partial v}{\partial y}. \tag{2}$$

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* Lamb, 'Hydrodynamics,' p. 548 (1924).

But there is no slip over the solid and the axes of x and y are tangential. Hence both terms on the right are zero. Thus both w and its first normal derivative vanish on the boundary. Also within the boundary layer $\partial^2 w/\partial z^2$ is nearly $-\partial^2 u/\partial x\partial z$. But $\partial u/\partial z$ is of order U/l, and therefore $\partial^2 u/\partial x\partial z$ is of order U/lc. Thus within the boundary layer

$$w = O\left(\tfrac{1}{2}\frac{U}{lc}z^2\right) = O\left(\frac{Ul}{2c}\right) \qquad (3)$$

at most. It is assumed, of course, that the velocity just outside the boundary layer is not large compared with U. It follows that at a distance l from the boundary the inclination of the actual velocity to the boundary is of order l/c. If then l/c and l/d are small, the motion is irrotational except within a layer whose thickness is small compared with d, and the velocity is nearly parallel to the boundary. Thus the conditions assumed by classical hydrodynamics are reproduced, in the specified conditions, by the real fluid. The two characteristic numbers are of order $(\nu/cU)^{\frac{1}{2}}$ and $(\nu c/d^2U)^{\frac{1}{2}}$. For an aerofoil of chord 100 cm., thickness 10 cm., moving in fluid of kinematic viscosity 0·1 cm.^{2}/sec. with velocity 10^3 cm./sec., these numbers are 10^{-3} and 10^{-2} respectively. But in such conditions as flow in a capillary tube l may be comparable with or larger than the diameter of the tube; then the whole of the fluid is effectively in the boundary layer and the classical conditions have no application. Similarly, for a sphere the conditions break down if Ua is as small as ν, where a is the radius. This is important, because it is in these conditions that the solutions of Stokes and Oseen have their application.

In any case, the classical solution cannot hold on the sheltered side, for a reason given, in its application to a sphere, by Prandtl.* In classical flow the fluid strikes the solid on the front, and there is a point on the boundary from which the fluid spreads out in all directions. Each stream line there is turned through a finite angle towards the fluid; the velocity therefore is zero and the pressure is $p_0 + \frac{1}{2}\rho U^2$, where p_0 is the pressure at a great distance. Similar arguments apply to the place on the rear where the fluid leaves the solid. The history of a portion of fluid that touches the solid is therefore that it starts with zero velocity, is accelerated by the pressure gradient up to the position of maximum velocity, and then has just enough kinetic energy to carry it against the pressure gradient to the rear point of stagnation. The modifications for fluid that only passes near the solid are evident. But in the real fluid the boundary layer is delayed by friction all the way round, and therefore would have insufficient energy to reach the rear point of stagnation even if there was one. The slowly moving fluid of the boundary layer can only come together behind the solid if the pressure is less than $p_0 + \frac{1}{2}\rho U^2$; and even if it is, this fluid must form a sheet or pencil, which prevents the irrotationally moving fluid from converging. There must therefore in any case be a wake with vorticity; and this vorticity must be allowed for in determining the motion of the irrotational fluid.

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* **‘Verh. Int. Math. Kongr.,’ Heidelberg (1903).**

We have therefore to choose between two alternatives. Either the pressure on the sheltered side in the fluid moving irrotationally approaches $p_0 + \frac{1}{2}\rho U^2$ somewhere, or it does not. In the former case, the fluid will approach this point and there leave the neighbourhood of the solid. Close to this point its velocity will be small. We should then have a wake whose thickness would at first be comparable with l in two-dimensional motion. In the latter case, the velocity will never become small, since Bernoulli's equation is applicable throughout the region considered. It follows that the fluid must leave the boundary tangentially. For if it did not, it would have to turn through a finite angle inwards towards the body of the fluid, and this implies a zero velocity. On the rear side the irrotational fluid is therefore bounded on the inside by a stream surface touching the solid where it meets it. In the wake just inside the angle of contact the velocity is evidently small, because fluid approaching the angle has to reverse its direction of motion to get away from it again. Thus there is a finite discontinuity of velocity across the stream surface.

4. The latter alternative is the one that agrees with experiment.* It is also consistent, so far as we have gone, with the free stream-line theory, according to which the wake would consist of a region of stationary fluid stretching to an infinite distance, and separated from the region of irrotationally moving fluid by a sheath of discontinuity of velocity. But there are several reasons why the free stream-line solution cannot be final. It makes the pressure in the wake, just behind the solid, equal to p_0; as a matter of experiment it is less than p_0. Theoretically also the surface of discontinuity cannot persist; it is equivalent to a local infinite vorticity, which must diffuse towards both sides and tend to smooth out the discontinuity. Also, apart from the effect of viscosity, a surface of discontinuity of velocity is unstable and would develop waves of large amplitude. Attempts have been made to explain what happens by means of the last consideration; but it seems to be inadequate by itself. To simplify matters, consider a plane sheet of discontinuity of velocity, and

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* Prandtl, 'J. R. Aeronaut. Soc.' (1927), figs. 25–28.

take the velocities above and below it to be $\frac{1}{2}U$ in opposite directions. Imagine the surface of separation deformed into a series of similar waves. Then wherever the surface projects into the upper fluid the velocity of the upper fluid is increased and that of the lower diminished, by considerations of continuity ; hence the changes of pressure resulting tend to push the lower fluid further into the upper. But if each wave is symmetrical about its crest, the distribution of pressure is also symmetrical. Therefore each wave must grow symmetrically, whatever its amplitude.* This is not what is observed. Surfaces of discontinuity of velocity do not give symmetrical waves of large amplitude ; they give series of vortices. What seems to happen when, by any means, a surface of discontinuity of velocity is produced in a fluid is that it continues approximately as a sudden transition of velocity for some distance and then generates vortices one by one at the free end. It must be noticed that theoretically both the viscous effect and the instability take time to grow, and apparently the viscous one is the first to become important. There seem to be reasons why elongated vortices might be expected to become circular ones under the influence of viscosity, but I know of no full investigation. In any case it happens. Then instability operates. A single row of vortices is unstable, as has been proved by von Karman.† But the nature of the instability is important, for the mode of disturbance that grows most rapidly is the one that in time becomes dominant. This mode is such that consecutive vortices are displaced in opposite directions. When the vortices arise from fluid moving with a finite velocity of slip over stationary fluid, the result is that half the vortices are swept into the dead water, where they produce a steady circulation. This appears to be the explanation of the reverse current often seen at the lee side of a corner projecting into a stream.‡ When the solid is very elongated in one direction at right angles to the direction of the stream, so that the motion is nearly two-dimensional, it seems probable on this ground that half the vorticity on each side of the wake is swept into it, and as the vorticities from the two sides are in opposite senses they ultimately annihilate one another through viscosity,§ meanwhile maintaining an eddying motion in the wake. The surviving vorticity is confined originally to the small proportion of the fluid that has traversed the boundary layer. By some imperfectly understood process this collects into isolated vortices in two rows ; the motion elsewhere is necessarily cyclic irrotational, because the rest of the fluid has never been near the solid. The vortices settle into the only steady two-dimensional arrangement in two rows that is not unstable, the asymmetrical double row of von Karman.* As this advances, the vortices spread out and ultimately annihilate one another. The time needed for this would be expected to be of order b^2/ν, where b is the width of the street and is of the same order in practice as d. The distance travelled by the vortices meanwhile is of order $\mathrm{U}b^2/\nu$, and the number in one row existing at one time is therefore of order $\mathrm{U}b^2/\nu a$, where a is the interval between consecutive vortices and equal to about $4b$. If then $\mathrm{U}b/\nu$ is large compared with 4, the Karman street can be a valid approximation to the truth. This condition is implied if the two characteristic numbers relating to flow near the solid are small, namely, $\nu/c\mathrm{U}$ and $\nu c/d^2\mathrm{U}$. Our discussion of the motion near the solid is therefore consistent with the representation of the wake by a well-developed Karman street.

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* This argument was communicated to me privately by Prof. G. I. Taylor.

† 'Phys. Z.,' vol. 13, pp. 49–59 (1912).

‡ 'Nature,' vol. 122, p. 206 (1928).

§ Suggestion made privately by Mr. H. Glauert.

The solution in the wake is then an irrotational motion without discontinuities except at the isolated vortices, which have derived their vorticity from the boundary layer. No place is provided for the fluid that must exist within the sheath of discontinuity and just behind the solid. Yet this fluid had a velocity differing by a finite amount from that of the fluid just outside the sheath, and if it was swept away in the wake this difference would be shown in the vorticity. Its width just behind the solid, we must remember, is comparable with the transverse dimensions of the solid, and if it came away with the vortices it would be impossible to regard the vorticity as confined to thin filaments. We have seen that the irrotational fluid leaves the solid tangentially; thus the sheath at first slopes inwards. It may be that it actually nearly closes up a little behind the solid, so that the fluid actually travelling away in it per unit time is very small in amount and hardly affects the motion of the rest. Alternatively the sheath just behind the solid may be quite wide, but the fluid within it may never leave the proximity of the solid. The relative motion close to the solid must in any case be small. The truth is probably intermediate. This fluid has a very slow general motion, so that the amount of it washed away in a given time is small compared with the whole amount in the wake, and it will mix with the irrotational fluid till it is indistinguishable either directly or by its effects.

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* This is not strictly correct, because L. Rosenhead has recently shown that, when allowance is made for the finite thickness of the vortex filaments, the Karman street is unstable for some three-dimensional disturbances. But the instability is slight when the vortices are thin, as they are initially.

5. An exceptional case arises where the solid has a corner projecting into the fluid. If the motion near the corner was irrotational, the velocity would become infinite there. But in the real fluid the slip velocity is zero on the solid, near the corner as everywhere else. Where the curvature of the boundary is finite we can find a vortical motion in the boundary layer, which, superposed on the general irrotational flow, will give the correct boundary conditions; for such a motion does tend to zero within a small distance from the boundary. But at a sharp angle this vortical motion involves infinite velocities, and there is no apparent reason why it should become inappreciable within a short distance from the corner. From this consideration alone we might expect our usual prediction that the motion is approximately irrotational except near the boundary to break down when there is a projecting corner. (An internal corner gives no trouble because the irrotational solution there gives zero velocity.) As a matter of experiment, we know that the irrotational solution does break down; the fluid fails to turn the corner at all, but comes off smoothly and leaves nearly stagnant fluid in the sheltered region. This solution does satisfy our conditions, for it is irrotational everywhere except along the surface where the two types of motion meet; and on this surface of transition we are dealing with fluid that has passed near the boundary and would therefore be expected to show great vorticity.

This consideration provides an explanation of the circulation theory of aeroplane lift. On the classical theory, when a body of aerofoil section is in a steady current, there is a point of stagnation some distance above the trailing edge, and the fluid has to turn this edge. The real fluid cannot do this, but comes off smoothly at the trailing edge. But the top of the body is of stream-line form, and we have seen that, if fluid passing over the top leaves the surface anywhere, it must do so tangentially. Hence even if it does leave the surface it must pass near the trailing edge, merely on account of the form of the solid; the wake is therefore necessarily thin. Outside the wake the motion is irrotational, and the effect of the wake is small. The only possible description of the motion that will satisfy the conditions outside the boundary layer is that it is irrotational, but the fluid leaves at the trailing edge instead of having a point of stagnation above it. This can be done only by superposing on the classical flow a cyclic irrotational flow, with just such a circulation around the aerofoil as will keep the velocity at the trailing edge finite.

If the wing is at such an angle of attack that the fluid leaving the surface on the upper side does so on the curved portion near the leading edge, the condition that it leaves tangentially no longer implies that it passes near the trailing edge, and the wake may be broad. This corresponds to the conditions of stalled flight.

In Joukowsky aerofoils, the wing has a cusp at the trailing edge, and the velocity of the fluid when it leaves is finite. In actual aerofoils, for reasons of construction, the angle at the trailing edge is finite, though small. But in any case this angle is in the wake and the velocity of the fluid relative to the solid is small. It appears that in actual conditions there may be little difference between the behaviour of wings with cusps and those with finite small angles at the tail.

6. It remains to be seen how far the ordinary theory of vortex motion, as given, say, in Lamb's 'Hydrodynamics,' corresponds to the theory just given of the generation of vorticity in real fluids. This theory rests on the motion of vortex lines, defined by the condition that the tangent to the vortex line at any point is in the direction of the resultant vorticity. This direction is everywhere definite except where the vorticity is zero, and the existence of vortex lines is a mere instance of the proposition that a differential equation has a solution. A vortex tube is defined as the locus of the vortex lines through a closed curve in the fluid, and it is proved that the circulation around any circuit embracing the same vortex tube is the same. It is inferred that a vortex tube cannot end blindly within the fluid, but must either go to infinity, end on a boundary, or be re-entrant.

The remarkable thing about this theorem is that we seem to have obtained a physical result out of nothing but pure mathematics. The fact seems to be that the theorem is true; but it is usually interpreted, I think, though not explicitly, to mean that regions where vorticity is present have the same property; and this is not an equivalent proposition. It is evident that, with any distribution of vorticity whatever, the argument could be developed equally well. Imagine, for instance, what would ordinarily be considered a vortex tube ending blindly at both ends, namely, a cylinder of finite length within the fluid rotating on its axis like a rigid body, and with the fluid outside it at rest. Then a little consideration shows that the vortex lines within the cylinder run parallel to the axis from end to end. At the ends they turn outwards and run along the ends to the circumferences of the ends; and the vorticity on the curved boundary where the rotating fluid meets the stationary fluid has its axis along the generators. Thus each vortex line runs parallel to the axis within the cylinder, out along the face when it meets the end, back along a generator, and in along the other face. It is a closed circuit, and the mathematical theorem is verified; but the physical result that it is often supposed to imply is untrue.

The existence of discontinuities in the velocities does not affect the argument; we could, if we liked, apply it to the motion that would replace this in a real fluid after a short time.

Again, suppose that the distribution of vorticity is given by

$$\frac{\partial w}{\partial y}-\frac{\partial v}{\partial z}=\xi;\quad \frac{\partial u}{\partial z}-\frac{\partial w}{\partial x}=\eta;\quad \frac{\partial v}{\partial x}-\frac{\partial u}{\partial y}=\zeta, \tag{1}$$

where (ξ, η, ζ) are supposed specified throughout the fluid. Then a solution is shown to be

$$u=\frac{\partial H}{\partial y}-\frac{\partial G}{\partial z};\quad v=\frac{\partial F}{\partial z}-\frac{\partial H}{\partial x};\quad w=\frac{\partial G}{\partial x}-\frac{\partial F}{\partial y}, \tag{2}$$

where

$$F=\frac{1}{4\pi}\iiint\frac{\xi}{r}\,d\tau,\ \text{etc.}, \tag{3}$$

$d\tau$ denoting an element of volume and (ξ, η, ζ) the vorticity there, and r the distance from this element to the place where (F, G, H) are to be found.

That this solution gives the proper vorticities everywhere is a matter of pure mathematics, subject to the convergence and differentiability of the various integrals. It has nothing to do with the mechanical properties of the fluid. But it is obviously only a particular integral of the equations (1); any irrotational motion could be superposed on it without affecting them. It is actually the solution that is valid when there is no divergence anywhere, and there is no boundary at a finite distance. If divergence is present, we must add on an irrotational solution to allow for it. If there is a boundary, we must add on a further irrotational and non-dilatational solution to annul the normal velocity there. In a real fluid we must also allow for the boundary layer near the solid.

The direct interest of this solution is not very great when the vorticity is generally distributed, for the differential equations satisfied by the vorticity contain the velocities explicitly through d/dt. Hence they contain more variables than the original equations satisfied by the velocities, and we might as well treat these directly. But when the vorticity is not generally distributed, but is confined to isolated regions within the fluid, the solution is of practical importance because it helps us to find the motion outside the regions of vorticity. This is especially true when these regions take the form of thin filaments. But these are precisely the circumstances that arise in the wake of a solid with real fluid moving past it.

In these cases, however, it appears to be preferable to treat the question from another aspect. In a real fluid with vorticity anywhere, after a short time there is no region where the vorticity is rigorously zero. But the vorticity at any place contains a factor exp $(-z^2/4\nu t)$, where z is the shortest distance of the particle from a solid boundary at any time during its previous path, and t is the time since the particle passed the front of the solid. The other factor, when the exponent is not small, is a power of z, usually negative, with others of order unity. If we take a circuit in the fluid, the circulation about it is the surface integral of the normal component of the vorticity over any surface that fills it. Two cases arise. Such a surface may pass through a region where z is small and the vorticity great; then we can infer nothing about the circulation in the circuit. This is equivalent to saying that there may be a circulation in any circuit that surrounds the wake or a part of it. But if the largest and smallest values of z on the contour or a circuit filling it are z_1 and z_0, and r is the actual distance of a point from the centre of the wake, the circulation Ω is given by

$$\begin{aligned}\Omega &= \iint (l\xi + m\eta + n\zeta)\, dS \\ &= O\left\{\int_{z_0}^{z_1} z^p\, e^{-z^2/4\nu t}\, dr\right\} \\ &= O\left\{{z_0}^{p+1}\, e^{-{z_0}^2/4\nu t}\right\}, \qquad (4)\end{aligned}$$

since z and r are comparable for points that have not passed close to the solid. Here p is a small number. It follows that, if the circuit can be filled by a surface such that no particle in it has passed within a distance of the solid comparable with $2(\nu t)^{\frac{1}{2}}$, the circulation about the circuit is negligible, on account of the smallness of the exponential factor. Now if we take two circuits such that we can find a surface connecting them, no particle on which has passed within such a distance of the solid, the two circuits can be connected by two paths on the surface, and we can apply the last result to the circuit composed of the two original circuits, described in opposite directions, and the two connecting paths. In the limit, we can then make the connecting paths indefinitely close together, and infer, by a familiar process, that the circulations about the two original circuits are equal save for a quantity of order given by (4). In the cases, therefore, where the concept of vorticity is capable of facilitating the discussion of the motion, we can say, with any desired accuracy, according to our definition of the term *near*, that—

1. If a circuit can be filled up by a surface, no particle on which has passed near the solid, the circulation about that circuit is insignificant; but if a circuit cannot be so filled up there may be a finite circulation about it.

2. If two circuits are such that they can be connected by a surface no particle on which has passed near the solid, the difference between the circulations about the two circuits is insignificant.

These two propositions constitute the physical basis of the application of the theory of vorticity to real fluids. For when the vorticity is confined to the neighbourhood of a curve in the fluid, and we require the velocity at such a distance away from the curve that we can neglect the variation in r in (3), we can put

$$d\tau = dx\,dy\,dz, \tag{5}$$

$$\iint \xi\,dy\,dz = \kappa_1, \tag{6}$$

where κ_1 is the circulation about a circuit in a plane of x constant enclosing all the vorticity in that plane. Then

$$\mathrm{F} = \frac{1}{4\pi}\int\frac{\kappa_1 dx}{r}; \quad \mathrm{G} = \frac{1}{4\pi}\int\frac{\kappa_2\,dy}{r}; \quad \mathrm{H} = \frac{1}{4\pi}\int\frac{\kappa_3\,dz}{r} \tag{7}$$

with an obvious notation. But when the vorticity is confined to such a region any two circuits embracing it have the same circulation, by the second proposition above. It is immaterial for what value of x the circulation κ_1 is determined; it is also immaterial whether the enclosing circuit is in a plane of x constant, one of y constant, or one of z constant. Hence

$$\begin{aligned}\kappa_1 = \kappa_2 = \kappa_3 &= \text{constant},\\ &= \kappa,\end{aligned} \tag{8}$$

where κ is the circulation in *any* circuit enclosing this region of vorticity. Thus we have the usual forms for the vector potential and therefore of the velocity due to a thin tube of vorticity. But they are now based on the physical properties of a real fluid and not on the mathematical conceptions of vortex lines and tubes, which have nowhere appeared in the argument.

The proposition that a vortex generated by the motion of a solid in a real fluid cannot end blindly within the fluid follows simply. For if it was possible, we could take a circuit near the end and fill it up by two surfaces, one passing inside the vortex and the other outside it. On the latter the vorticity is everywhere zero and therefore the circulation about the circuit is zero. Therefore the circulation about the alleged vortex is zero. We infer that a vortex is either re-entrant, ends on a boundary, or goes to infinity; and the circulation about it is everywhere the same.

The irrotational motion about a vortex or set of vortices necessarily has a velocity potential Φ; but this function is cyclic, since whenever we move round a vortex back to the same point it increases or decreases by κ. The three different types of vortices correspond to differences in the behaviour of Φ at a great distance. If a vortex extends to infinity, then we can take a point on its axis at any distance from the origin and there draw a plane normal to the axis. When we go round the axis in that plane Φ increases by κ. Hence if we take an azimuthal angle ϕ in that plane $\Phi - \frac{\kappa}{2\pi}\phi$ is non-cyclic. Thus Φ contains a cyclic part involving an angle, but not containing a power of the distance as a factor. It is therefore a spherical harmonic of zero order.

If a vortex ends on boundaries at both ends, (F, G, H) at great distances are of order $1/r$, (u, v, w) of order $1/r^2$, and Φ of order $1/r$. The velocity potential therefore is a solid harmonic of degree -1.

But this does not appear to be a practical case, for a circuit surrounding the vortex would have a circulation about it; but it could be filled up by a surface passing beyond the solid, and then would have no circulation.

If there is no vorticity beyond a certain finite distance from the origin, which is the ordinary practical case, we can draw a sphere of radius a such that all the vorticity is within it. Then there is no circulation about any circuit on the sphere, and such integrals as $\iint \xi \, dy \, dz$ over plane sections of the sphere vanish. Hence at points outside the sphere

$$\mathrm{F} = \frac{1}{4\pi}\iiint \frac{\xi}{r}\, dx\, dy\, dz$$

has a value different from zero only on account of the variation of r; and for points remote from the centre it is therefore of order

$$\frac{1}{4\pi} \cdot \frac{a}{r^2} \cdot \tfrac{4}{3}\pi a^3 \, \xi_{\max.} \quad \text{or} \quad \tfrac{1}{3}\frac{a^4}{r^2}\, \xi_{\max.}$$

Thus Φ must be a harmonic of order -2, as for a doublet. This is what we should expect, since a vortex ring, like a doublet, is a place where fluid enters on one side and is ejected on the other.

6. In two-dimensional flow, considerable success has been obtained in relating the forces on solids to those inferred from theories of cyclic irrotational flow. Several attempts have been made to adapt the two-dimensional theory to various cases of three dimensional motion. The most successful is the allowance for finiteness of wing span in finding the drag of an aerofoil, due in general terms to Lanchester and in its development to Prandtl and his followers.*

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* *Cf.* Glauert, 'Aerofoil and Airscrew Theory,' 1926.

If we take any vertical line behind the aeroplane and running through the wake, we can form a circuit containing it by forming a loop from its ends and passing either in front of the wing or to one side of the wake. The fluid between these two loops has not passed near the solid. The two circuits are therefore reducible without passing through fluid with vorticity; on the only part of them where there is vorticity they are identical. Hence the circulations about the two circuits are equal. There must therefore be two vortices trailing from the ends of the wing, effectively with circulations equal to that about the aerofoil. Behind the wing these influence each other; each twists up into a bundle of vortex filaments, and each acquires a general downward velocity. The energy involved in drawing out these vortices as the machine advances accounts for a large fraction of the resistance to its flight.

When the dimensions of the solid in the two transverse directions are comparable, and in particular for a solid of revolution with its axis in the direction of the general motion, it appears to be probable that there is no quasi-steady motion that will represent the wake. In two dimensions, the Karman street* represents the facts; I call it quasi-steady rather than steady because the vortices move with a velocity intermediate between those of the solid and the distant fluid; but there is a velocity such that, if we take a point moving with it, the pattern in the wake remains fixed with respect to it until the vortices spread out through viscosity. In three-dimensional flow, the natural course would be to try to generalize the Karman street. If each vortex bent round at the ends and joined on to the two neighbouring ones of the other row, the Karman street would become a single vortex with a helix for its axis. The stability of the helical vortex has been proved in certain conditions by H. Levy and A. G. Forsdyke.† But it cannot represent the actual motion. Suppose that the general direction of the flow, and the axis of the helix, are along the x axis, and consider a circle in a plane perpendicular to the x axis, with a radius several times the radius of the helix or the transverse dimensions of the solid. The fluid on this circle has never passed near the solid, and therefore the circulation about it is zero. But the circle can be filled up by a surface cutting the helix once, and the circulation about it is equal to the strength of the vortex itself. We have therefore a contradiction. A single helical vortex is not a possible wake.

Prof. Levy has suggested‡ very tentatively that there might be a quasi-steady motion consisting of a helical vortex with another vortex of equal and opposite strength along its axis. This avoids the last difficulty. But it is very difficult to see how such a central vortex can be maintained. The vorticity in any case springs from a sheath of discontinuity with the greater velocity on the outside. The axis of the vorticity on this sheath is necessarily perpendicular to the general direction of flow. To make the helical vortex, it has to be turned round through a constant angle, the pitch of the helix; and it must be carried away with the general velocity of the helix. The vorticity on the axis might then be maintained by the separation into two parts of the vorticity developed from the sheath, one part drifting along the cylinder while the other goes to the axis and moves down that, the axis of the vorticity meanwhile being turned through a right angle. The possibility of such a process seems very doubtful; perhaps the most difficult part to accept is the idea of separating the vorticity that originates at one place into two parts, seeing that the usual tendency of vortices is to diffuse out and coalesce. The alternative mechanism seems to be that the whole of the vorticity passes down the helix, but turns round and comes back along the axis. This can take place only when the vortex is far enough from the solid to be losing its helical character through viscosity, and therefore the axial vortex developed from it can hardly be of a very regular character. Further, if it brings the whole of the vorticity back to the neighbourhood of the solid, there is no place for the newly generated vorticity to go to.

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* *Cf.* Karman and Rubach, *loc. cit.*; also H. Bénard, 'Comptes Rendus,' vol. 147, pp. 839–842, 970–972 (1908).

† 'Roy. Soc. Proc.,' A, vol. 120, pp. 670–690 (1928).

‡ 'Aero. Res. Ctee.,' T.2921, March, 1930.

There are two possible ways of combining helical vortices so as to keep the circulation zero about a circle drawn in the fluid that has not been near the solid. Two helices may be wound on the same cylinder. If they twist in opposite senses, they intersect twice in each turn about the axis of the helix. Where they intersect each gives an infinite (or in practice very large) velocity of rotation to the other, and the motion is not quasi-steady. If they twist in the same sense and do not intersect, we have two parallel helices on the same cylinder with the vorticity in the one just balancing that in the other. But then it is not obvious that the system constitutes a steady motion. Even if it does, the velocity of the helices induced by one of them will counterbalance that due to the other, and the system will not move at all; and the average generation of vorticity from any given portion of the margin of the solid is zero. But the stream-surface from the margin is in any case effectively a surface of discontinuity of velocity, with the difference between the velocities just inside and just outside always in the same sense; there must be a systematic generation of vorticity in one sense, which is carried away by the vortices breaking away from the slip-surface.

It appears therefore that the wake cannot consist of a helical vortex or a combination of two helical vortices.

Another possible generalization of the Karman street is that each vortex may bend round and connect up at the ends with the *same* vortex of the other row. Thus we should have a series of vortex rings. But the plane of each ring would not be at right angles to the axis of the wake, and the rings would therefore drift out of the wake. The only possible solution in terms of vortex rings would be a row of rings with their planes perpendicular to the axis of the street. This is a possible quasi-steady motion, but Levy and Forsdyke have proved that it is unstable.* It appears therefore that there is no stable quasi-steady motion that will represent the wake in three dimensions. Even this unstable solution is not an analogue of Karman's street, which is an asymmetrical double row, but of the symmetrical double row in two dimensions, which is well known to be unstable in theory and not realized in experiment.

The belief that the Karman street cannot be generalized to three-dimensional motion is indicated also by the flow past an aerofoil of finite span, which represents the smallest possible departure from the two-dimensional case. The flat wake generates a number of vortex filaments, with their axes at *small* angles to the general direction of flow, and twisting about one another in a wildly irregular manner. The motion even in this case is not a small modification of the Karman street, but a radically different motion.

Further, it has been shown by L. Rosenhead,† that the two-dimensional Karman street in an infinite region of fluid is always unstable for three-dimensional disturbances when the vortices are of finite thickness, as they must be in practice.

It appears therefore that the vortices generated in three-dimensional flow, even when the two-dimensional flow is a useful first approximation to the facts in a limited region, do not form a system drifting steadily down-stream, and there is no simple extension of the Karman street to three dimensions. When the solid is approximately one of revolution, with its axis along the general direction of flow, there is a quasi-steady solution in terms of a series of vortex rings drifting down-stream ; but this is unstable and in any case is not an analogue of the Karman street. The actual motion in the wake is probably completely turbulent.

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* 'Roy. Soc. Proc.,' A, vol. 114, p. 594 (1927).

† 'Roy. Soc. Proc.,' A, vol. 127, p. 590 (1930).

The Kinetics of the Oxidation of Copper. Part I.—*The Initial Oxidation of Copper at Low Pressures.*

By F. J. Wilkins and E. K. Rideal.

(Communicated by T. M. Lowry, F.R.S.—Received March 10, 1930.)

The oxidation of copper has been the subject of several investigations. It was first treated quantitatively by Pilling and Bedworth* in their study of the oxidation of metals. They showed that metals, in so far as the kinetics of their oxidation is concerned, may be divided into two classes, according as the oxide occupies a greater or less volume than that of the metal from which it is formed. In the first case it is clear that the oxide will protect the remaining unoxidised metal from attack, while in the second, owing to the necessarily porous nature of the oxide no such protective action can arise. Copper belongs to the first group. Pilling and Bedworth pointed out that when the oxide protects the metal, as soon as a complete oxide layer is formed, the factor controlling the rate of oxidation is the rate of diffusion of oxygen through the oxide. If now it is assumed that the rate of diffusion is inversely proportional to the thickness of the oxide layer, then we may write

$$dx/dt = k/x, \tag{1}$$

where x is the weight of oxide formed at time t and k a constant.

Integrating we obtain

$$x^2 = kt. \tag{2}$$

This equation was found to describe the rate of oxidation of metals belonging to the first group accurately. Copper, however, provided an exception; for, although the increase of volume accompanying oxidation is in the ratio of 1 to 1·67, it was only at high temperatures that the oxidation process followed equation (2). At lower temperatures the rate of oxidation varied in a capricious manner with time. This was attributed to the cracking of the oxide film.

More recently, Dunn† has reinvestigated the low temperature oxidation of copper. He finds that between 200° and 300° C. the oxidation of commercial copper follows (2) over short ranges of time. The behaviour of copper activated by oxidation and reduction was, however, anomalous. The results could not be expressed by (2) even over the shortest ranges of time.

* ‘J. Inst. Metals,’ vol. 29, p. 529 (1923).

† ‘Roy. Soc. Proc.,’ A, vol. 111, p. 210 (1926).

The high temperature oxidation of copper has been further studied by Feitknecht.* He found that for oxidation at 850°, 950° and 1020° C. the constant k of (2) gradually decreased to a constant value. He suggested that this decrease was due to sintering which rendered the oxide more impermeable to diffusing oxygen. A closer analysis† of his results has shown, however, that they obey the parabolic law in the more general form,

$$x^2 = kt + c. \tag{3}$$

We may, therefore, conclude that under these conditions the rate of oxidation of copper is governed by the rate of diffusion of oxygen through the film of oxide ; a result in accord with those of Pilling and Bedworth, and Dunn.

The problem which immediately arises is the nature of the diffusion process. Dunn has made the following suggestion. He supposes that—

(1) "the structural units of the oxide are in a state of vibration and that a random distribution of the energies of vibration prevails" ; and

(2) "that an oxygen molecule can only pass a structural unit provided that this possesses at the moment energy greater than the critical, causing a loosening of the oxide structure at that point." While he was unable to specify the type of structural unit involved—whether the ion or the molecule—the concept of the diffusion process which emerges clearly from these assumptions is the passage of the oxygen molecule through the cuprous oxide lattice. Feitknecht (*loc. cit.*), on the other hand, has stressed the view that the diffusion of oxygen occurs mainly along grain boundaries of the oxide rather than through the lattice. He came to this conclusion because he had noticed that the decrease in the value of k was accompanied by an increase in grain size. In view of the later analysis of his results, however, this evidence must be discounted.

Lattice Diffusion.

From simple consideration of the dimensions involved, it is clear that lattice diffusion can play no part in the low temperature oxidation. Greenwood‡ has shown that the edge of the unit cubic cell of cuprous oxide is 4·28 Å. Taking the diameter of the oxygen ion as 2·7 Å.§ and neglecting the size of the copper ions, it can be shown that there is not sufficient room for an oxygen molecule of diameter* 3·62 Å. to pass through a stable lattice. At high temperatures (1000° C.), however, when the lattice is much less stable—cuprous oxide melts at 1235° C.—there are no *a priori* reasons against lattice diffusion. Experimental evidence supports these considerations. It has been shown that Feitknecht's figures fit the parabolic equation in the more general form, and that therefore the permeability of the oxide film towards oxygen remains constant. Feitknecht demonstrated that during the oxidation sintering of the oxide film occurred, the grain size increasing considerably. It is clear, therefore, that while grain boundary diffusion must exist, most of the oxygen diffuses through the lattice.

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* 'Z. Elektrochem.,' vol. 35, p. 142 (1929).

† Wilkins, 'Z. Elektrochem.,' vol. 35, p. 500 (1929).

‡ 'Phil. Mag.,' vol. 48, p. 653 (1924).

§ Bragg and West, 'Roy. Soc. Proc.,' A, vol. 114, p. 450 (1927).

Grain Boundary Diffusion.

The granular structure of solids, apparently continuous has often been demonstrated.† Zwicky,‡ in particular, has shown that the lattice spacings of a two-dimensional lattice are smaller than those of the corresponding three-dimensional lattice, in consequence of which the surface of a solid will tend to contract. Since the surface cannot contract as a whole, it will do so in patches of definite average size between which cracks will be left open. He points out further that the crystal will not only crack on the surface but will also exhibit a great tendency towards block formation.

Direct evidence of the granular structure of cuprous oxide films has been obtained by Feitknecht (*loc. cit.*). He has shown by means of an X-ray analysis of films formed on copper at 183° C. that the grains (assuming them to be spheres) were greater than 10^{-6} cm. but less than 10^{-4} cm. in radius. Bragg§ is also of the opinion that activated nickel consists of crystals of colloidal dimensions. Activation of copper by alternate oxidation and reduction will be accompanied by a decrease in size of the grains due to the disruptive action of the water vapour formed during the reduction.|| We have, therefore, a very simple explanation of the increased rate of oxidation of copper after activation. An explanation is also possible for the anomalous temperature coefficient noticed by Dunn (*loc. cit.*). He found that if $\log_e k$ was plotted against $1/T$ a set of points is obtained which appears to lie on two straight lines which pass into each other fairly sharply at about 660° C. We

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* Jeans, "Dynamical Theory of Gases," p. 327.

† For example, Smekal, 'Z. Tech. Physik,' vol. 8, p. 561 (1927).

‡ 'Proc. Nat. Acad. Sci.,' vol. 15, p. 253 (1929).

§ Private communication.

|| Guichard, Clausmann, and Billon, 'C. R.,' vol. 186, p. 1121 (1928).

may, therefore, conclude that the influence of temperature on the rate of oxidation is described by the equation

$$-d \log_e k/dt = Q/RT^2,$$

the temperature coefficient being determined by two different "heats of activation." From the earlier discussion such a result is to be expected. At high temperatures the "heat of activation" should be that of the predominating lattice diffusion; at low temperatures, that of the predominating grain boundary diffusion.

The high and low temperature oxidation of copper are, therefore, quite different problems. The research to be described is restricted to oxidation below 300° C.

The Rate of Oxidation as Controlled by Factors other than Diffusion.

The consideration of the oxidation of copper in terms only of the diffusion process, obviously represents an undue simplification of the problem. On *a priori* grounds, the rate of oxidation must be dependent on the rates of at least four processes :—

(*a*) The condensation of oxygen at the cuprous oxide/oxygen interface ;
(*b*) The evaporation of oxygen from the oxide/oxygen interface into the body of the oxide ;
(*c*) The diffusion of oxygen through the oxide ; and
(*d*) The reaction between oxygen and copper.

U. R. Evans* has generalised the treatment of the oxidation of metals, taking into account (*c*) and (*d*) only, by considering the case in which the rate of reaction at the oxide metal interface is of the order of the rate of diffusion.

He shows that (1) now becomes

$$dx/dt = k_0 k_1 C/(k_0 + k_1 x), \tag{4}$$

where k_0 is the diffusion coefficient of oxygen through the oxide, k_1 the mass action constant for the reaction between the metal and oxygen and C the concentration of oxygen at the oxide/oxygen interface. If k_0 is small, the rate of diffusion is the controlling factor and (4) reduces to (1). In the other limiting case, when k_1 is small, (4) becomes

$$dx/dt = k_1 C. \tag{5}$$

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* "Corrosion of Metals," p. 14.

This equation describes the oxidation of calcium, a metal which forms a porous oxide.

The object of the experimental work described in this paper was to consider, in particular, the influence of the process (a) on the rate of oxidation of copper by studying the oxidation at low pressures.

The low pressure oxidation has been studied already by Hinshelwood.* He heated copper at 305° C. in a closed system containing oxygen at pressures below 5 mm., and measured the rate of reaction by observing the fall of pressure. If p_0 is the pressure at time t, then since the volume of the system is kept constant, the thickness of the oxide film is proportional to $(p_0 - p)$. Equation (1) becomes, therefore,

$$d(p_0 - p)/dt = k/(p_0 - p), \tag{6}$$

and the parabolic equation

$$(p_0 - p)^2 = kt.$$

This equation does not hold. He, therefore, suggested that while the rate of oxidation was governed by the rate of diffusion through the oxide layer, the rate of diffusion was proportional to the pressure. He modified (6) and wrote

$$-dp/dt = kp/(p_0 - p)$$

which integrated to

$$t = 1/k\{p_0 \log_e (p_0/p - (p_0) - p)\}.$$

This expression did not fit his results at all well. The values of k showed a gradual drift throughout the course of an experiment, the difference between the initial and final values being as much as 60 per cent.

Experimental.

The experimental method is similar in principle to that employed by Hinshelwood (*loc. cit.*).

Pieces of copper foil 1 sq. cm. in area were cleaned by first abrading with emery paper and then washing with alcohol. They were finally subjected to prolonged rubbing with grease-free cotton wool. Oxide films formed during the course of the work were removed by reduction with hydrogen *in situ*. Oxygen was generated by heating pure potassium permanganate: hydrogen by the electrolysis of a solution of pure baryta containing a little caustic soda. Both gases were dried by passage over phosphorus pentoxide.

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* 'Roy. Soc. Proc.,' A, vol. 102, p. 318 (1922).

Diagrams, both of the first form of the apparatus and of the second improved form, are given in figs. 1, A and B. In the first form, the reaction chamber A containing copper was connected on one side to a manometer M, and, on the other, to a Töpler pump. Plugs of tin and gold foil were inserted at BB′ and CC′ respectively in order to prevent diffusion of mercury vapour from the manometer and pump to the reaction vessel. In spite of this it was found that after 5 or 6 weeks' use a piece of copper showed definite signs of poisoning. To get over this difficulty the apparatus was redesigned and a glass worm E silvered on the inside and surrounded with liquid air, was substituted for the plugs of tin and gold foil.

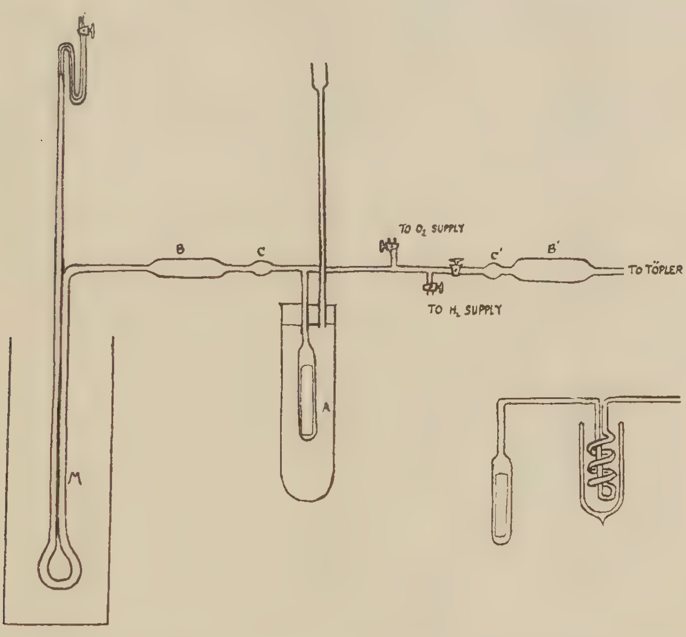

FIG. 1A.

FIG. 1B.

The majority of the oxidations was carried out at 183° C., the reaction chamber being immersed in the vapour of boiling aniline. At this temperature the sintering, even with active copper, was negligible over a period of as much as 1 hour. To obtain other temperatures suitable liquids were substituted for aniline.

Pressure Measurement.

All the oxidations were carried out at pressures below 10 mm. Since the pressure changes occurring during an experiment were small, great care had to be exercised in measuring them. The movements of the mercury column were measured by means of a travelling microscope clamped to a heavy iron stand. Movements of the column due to variations in the laboratory temperature were eliminated by placing the manometer in a thermostat. Further, any movements of the microscope relative to the manometer due to similar changes of temperature, were eliminated for all practical purposes by clamping the manometer and microscope to the same supporting stand. As one meniscus only could be read by the microscope, the manometer was calibrated for errors due to variations in the bore of the tube. By selecting the tubing carefully these errors could be made negligible except for very small pressures.

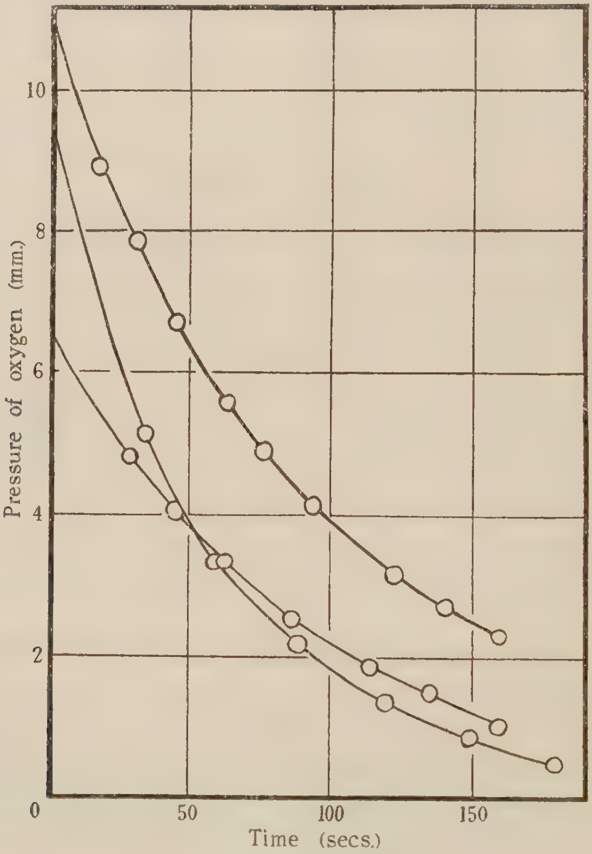

Fig. 2.—Examples of Pressure-Time Curves.

The results obtained with this apparatus were completely satisfactory. Fig. 2 gives examples of the type and smoothness of the pressure time curves obtained.

Experimental Results and Discussion.

(1) *The Low Pressure Oxidation at Constant Temperature.*—After a piece of copper has been activated by alternate oxidation and reduction, it is found that the oxidation at low pressures may be described by the simple equation

$$\log p_0/p = kt, \tag{7}$$

where p_0 is the initial pressure of oxygen, p the pressure at time t, and k is a constant.

Examples of the application of this equation to the results are given in Tables I to VI.

Table I.—Temperature of Oxidation = 183° C.

Time in seconds.	Pressure in mm. (observed).	Pressure in mm. (calculated).
18	7·42	7·41
37	7·03	7·03
61	6·63	6·64
83	6·24	6·27
103	5·90	5·96
128	5·55	5·56
160	5·12	5·14
187	4·80	4·80
221	4·41	4·40
254	4·08	4·04

Table II.—Temperature of Oxidation = 142° C.

Time in seconds.	Pressure in mm. (observed).	Pressure in mm. (calculated).
71	8·88	8·85
148	8·12	8·11
234	7·68	7·70
298	7·40	7·40
358	7·14	7·14
418	6·88	6·90
508	6·56	6·54

Table III.—Temperature of Oxidation = 209° C.

Time in seconds.	Pressure in mm. (observed).	Pressure in mm. (calculated).
11	10·38	10·38
22	9·88	9·86
32	9·46	9·44
53	8·62	8·65
69	7·98	8·07
86	7·46	7·52
100	7·08	7·15
116	6·60	6·65
139	6·06	6·04

Table IV.—Temperature of Oxidation = 218° C.

Time in seconds.	Pressure in mm. (observed).	Pressure in mm. (calculated).
22	5·96	5·57
34	4·81	4·76
43	4·08	4·12
56	3·34	3·34
61	2·60	2·62
84	2·18	2·15
99	1·62	1·62
113	1·24	1·27

Table V.—Temperature of Oxidation = 249° C.

Time in seconds.	Pressure in mm. (observed).	Pressure in mm. (calculated).
12	4·82	4·76
20	4·02	4·03
31	3·42	3·42
41	2·84	2·84
51	2·38	2·38
63	1·96	1·96
75	1·60	1·59
93	1·26	1·18

Table VI.—Temperature of Oxidation = 305° C.

Time in seconds.	Pressure in mm. (observed).	Pressure in mm. (calculated).
14	5·14	4·07
24	3·24	3·31
33	2·46	2·49
42	1·78	1·91
53	1·34	1·33
65	1·04	0·99

In order to make a more searching test of (7) the influence of p_0 on k was studied using a piece of copper of constant activity. The results show in accordance with (7) that k is independent of p_0, *e.g.*, for a value of $p_0 = 12 \cdot 76$ mm. k was found to be 0·0113, with $p_0 = 9 \cdot 35$ mm. k was 0·0112.

In all approximately 70 experiments have been carried out on active copper at low pressures during the course of this work, and only in one or two cases at the most has any serious divergence from (7) been found.

In spite of the accuracy with which this equation is obeyed when applied to the oxidation of active copper at low pressures it fails completely when applied to either—

(*a*) the oxidation of activated copper at high pressures ; or
(*b*) the oxidation of inactive copper at low pressures.

The former has been the subject of a special investigation which will be described in a later paper. The latter has revealed itself as an observation of considerable interest since (as will be shown later) it appears to provide evidence demonstrating the existence of lateral diffusion in adsorbed gas molecules.

An Analysis of the Kinetics of the Oxidation of Copper.

The extreme simplicity of the experimentally established equation is very surprising. It is obvious that it is of a type entirely different from the parabolic equation, and we may, therefore, conclude that we have to do here with a process other than that of diffusion.

Evans' (*loc. cit.*) hypothesis is the only one which admits of a mechanism of oxidation not governed by diffusion. It has been mentioned already that for the oxidation of a metal with a porous oxide, he had deduced the equation

$$dx/dt = k_1\mathrm{C}. \tag{5}$$

It has also been pointed out that activation is accompanied by a decrease in the grain size of the oxide. It might be suggested, therefore, that in spite of the increase of volume accompanying oxidation, the oxide formed on activated copper is porous, and the conditions satisfy (5). Transforming this into the form applying to oxidation in a closed system, we obtain

$$-dp/dt = kp$$

which integrates to

$$\log_e p_0/p = kt, \tag{7}$$

the expression found experimentally. While, however, this theory is able to provide the necessary relationship between pressure and time and in particular is able to explain why the oxidation of inactive copper does not satisfy (7), it is not entirely satisfactory. In the first place, it provides no explanation of the deviation from (7) at high pressures. In the second place, it has been shown (see Part II of this research) that at 183° and at pressures as high as 100 mm. that the parabolic equation is obeyed, even on activated copper. It is, therefore, evident that the concentration of free oxygen at the copper/copper oxide interface is even at high pressures quite negligible. The limiting case of Evans' equation is, therefore, inapplicable to this problem.

It has been suggested earlier, that the rate of oxidation of a metal is dependent upon four factors :—

(*a*) The rate of supply of oxygen to the metallic oxide/oxygen interface.
(*b*) The rate of removal of oxygen from the metallic oxide/oxygen interface into the oxide.
(*c*) The rate of diffusion of oxygen through the oxide.
(*d*) The rate of reaction between the metal and oxygen.

Since it has been shown that under the experimental conditions (*d*) is so rapid for copper and oxygen that it may be neglected, we may, as far as copper is concerned, treat the oxidation as the sum of the three consecutive processes (*a*), (*b*) and (*c*).

Now initially, and at sufficiently low pressures, the cuprous oxide/oxygen interface will be almost free from adsorbed oxygen, so that (*a*) will become so small compared with (*b*) and (*c*) that it will determine the rate of the reaction. In these circumstances, the equation describing the rate of oxidation is

$$-dp/dt = kp.$$

This analysis besides giving the required relationship between pressure and time also explains the deviations at high pressures, for, under these conditions, (*a*) becomes so large that it no longer determines the rate of reaction. In the introduction to this paper it was suggested that at low temperatures oxygen reached the copper/cuprous oxide interface by diffusion along the grain boundaries of the cuprous oxide. If now lateral diffusion of adsorbed oxygen takes place along the cuprous oxide/oxygen interface, the rate of evaporation of oxygen into the oxide, *i.e.*, (*b*) will depend upon the number of grain boundaries in unit area. On active copper this is large and in consequence (*b*) is rapid. Inactive copper, however, has a relatively large grain size and therefore (*b*) is slow. If (*b*) is slow enough (*a*) will no longer determine the rate of reaction and (7) will not be obeyed.*

The results of this analysis appear to show, therefore, that adsorption is a necessary preliminary to diffusion, and also that under the experimental conditions the oxide is practically denuded of adsorbed oxygen, *i.e.*, no adsorption equilibrium exists between the oxide/oxygen interface and the gas phase. The last result proved to be indispensable in the treatment of the high pressure oxidation.

The Temperature Coefficient of the Low Pressure Oxidation.

In order to determine the temperature coefficient a piece of copper was oxidised and reduced at 183° C. until its rate of oxidation as measured by the k of equation (7) was constant. Determinations of k were made over the temperature range 140°–300° C., with constant checks at 183°. The determination at 300° was always carried out at the end of a series in order to prevent sintering. It was found that the values of k which are given in the following table satisfied the equation

$$-d \log_e k/dT = Q/RT^2.$$

T° K.	1/T.	k.
415	0·00241	0·00053
460	0·00217	0·0019
483	0·00207	0·0030
515	0·00194	0·0058

Several runs were made on samples of copper of varying activity. The mean value of Q is 9500 cals., with an error of approximately 1000 cals.

It is interesting to note that the "heat of activation" for the diffusion of oxygen through cuprous oxide, as calculated from Dunn's figures, is also equal to approximately 9500 cals., over the temperature range below 600° C. In the earlier discussion we have attributed this figure to the heat of activation of the grain boundary diffusion. It is probable that not all the grain boundary will be able to allow the diffusion ; the existence of a temperature coefficient shows that this cannot be so. The heat of activation is, therefore, the critical increment of energy which " locker-stellen " on the grain boundary must possess before an oxygen molecule can diffuse. The temperature coefficient of the initial low pressure oxidation is on this view dependent upon the increase in the number of " locker-stellen " in the surface as the temperature is raised.

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* Evidence demonstrating this lateral diffusion has been obtained from the work at high pressures (see Parts II and III).

No experimental evidence exists to show in what form—molecular, atomic, or ionic—oxygen diffuses through cuprous oxide.* The low value of the heat of activation would appear to suggest that it is the molecular form of oxygen which is involved.

Summary.

It is suggested that the oxidation of copper is the resultant of three consecutive processes and that its velocity depends upon :—

(*a*) The rate of condensation of oxygen at the oxide/oxygen interface.
(*b*) The rate of removal of oxygen from the oxide/oxygen interface into the oxide.
(*c*) The rate of diffusion of oxygen through the oxide.

The initial oxidation at low pressures is governed by (*a*), and the equation describing the rate of oxidation is therefore

$$\log_e p_0/p = kt.$$

This equation does not hold for the oxidation of active copper at high pressures or inactive copper at low pressures.

Our thanks are due to Mr. C. Smith for assistance with the experimental work and to the British Non-Ferrous Metals Research Association for a grant to one of us (F.J.W.).

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* See, however, Palmer, 'Roy. Soc. Proc.,' A, vol. 103, p. 444 (1923).

The Kinetics of the Oxidation of Copper. Part II.—*The Limiting Pressure.** *Evidence for the Lateral Diffusion of Adsorbed Gas.*

By F. J. Wilkins.

(Communicated by T. M. Lowry, F.R.S.—Received March 10, 1930.)

Introduction.

The influence of the pressure of oxygen on the rate of oxidation of copper has been studied by earlier workers. Pilling and Bedworth† working at 800° C. found that the rate of oxidation continued constant as the pressure was decreased until the pressure reached 0·3 mm. Berger‡ found a limiting pressure of 100 mm. Hinshelwood's§ work makes it clear that for activated copper at 305° C. the limiting pressure is greater than 5 mm. Palmer|| obtained a value of about 300 mm.

The object of this work was to investigate more closely the significance of the limiting pressure.

Experimental.

The apparatus used and the experimental method employed were essentially the same as those described in Part I. All oxidations were carried out at 183°. This temperature was high enough to give convenient rates of oxidation and low enough (as the results show) to prevent the sintering, even of activated specimens of copper, becoming appreciable during the time of an experiment.

The Methods of Determining the Limiting Pressure.

The differential equation corresponding to the parabolic law becomes

$$d(p_0 - p)/dt = k/(p_0 - p)$$

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* The limiting pressure is that pressure below which the rate of oxidation ceases to be independent of the pressure of oxygen.

† 'J. Inst. Metals,' vol. 29, p. 529 (1923).

‡ 'C. R.,' vol. 158, pp. 1502, 1729 (1914).

§ 'Roy. Soc. Proc.,' A, vol. 102, p. 318 (1922).

|| 'Roy. Soc. Proc.,' A, vol. 103, p. 444 (1923).

when applied to the oxidation of copper in a closed system. Integrating between the limits t_1 and t_2 and arranging terms the linear equation

$$2k(t_1 - t_2)/(p_1 - p_2) = 2p_0 - (p_1 + p_2) \tag{1}$$

is obtained ; p_1 and p_2 are the pressures of oxygen in the system at t_1 and t_2 respectively.

First Method.—In the first method $(t_1 - t_2)/(p_1 - p_2)$ and $(p_1 + p_2)$ were calculated from the experimental results and plotted. The pressure at which departure from linearity was first observed was taken as the limiting pressure (see figs. 4 and 5).

Second Method.—The total pressure change in an experiment was only of the order of 10 mm. Unless one knew, therefore, to within 10 mm. the position of the limiting pressure, the first method was not suitable. Equation (1) allows us, however, to explore over a much wider range. An examination of it shows that the two terms to be plotted are independent of p_0, and that any arbitrary values of t_1 and p_1 could be chosen from the experimental results. It was the custom, therefore, when determining a limiting pressure whose position was unknown, to introduce or remove oxygen from the system at suitable intervals and choose new values of p_1 and t_1. An example is given below to illustrate the method.

Oxygen was introduced at t_0 and pressure and time readings taken. These are given in Table I.

Table I.

$p_0 = 30{\cdot}8$. $t_0 = 50' \, 19''$.

Time.		Pressure p.	$p_1 + p_2$ $p_1 = 26{\cdot}4$.	$t_1 - t_2/p_1 - p_2$ $t_1 = 50$.
min. sec.	sec.			
50 39	20	26·4		
50 55	36	23·80	50·20	6·16
51 11	52	22·22	48·62	7·65
51 28	69	20·94	47·34	8·98
52 5	106	19·34	45·74	12·18
52 27	128	18·43	44·83	13·56
52 47	148	17·93	44·35	14·79
53 13	174	17·26	43·66	19·03
53 33	194	16·86	42·26	20·33
54 15	236	16·22		
54 57	278	15·88		
55 36	317	15·58		

Fresh oxygen was now put in and a new series of readings taken beginning at 57′ 20″.

Table II.

Time.		Pressure p.	$p_1 + p_2$ $p_1 = 44 \cdot 37$.	$t_1 - t_2/p_1 - p_2$ $t_1 = 57' 20''$.
min. sec.	sec.			
57 20	0	44·37		
58 3	43	44·13	88·50	176·2
59 0	100	43·85	88·25	191·5
60 0	160	43·64	88·02	218·6
61 0	220	43·41	87·78	227·3
63 0	340	43·00	87·38	248·2
65 0	460	42·67	87·04	270·1

More oxygen was admitted and readings begun at $t_0 = 67$ minutes.

Table III.

Time.		Pressure p.	p_1+p_2.	$t_1 - t_2/p_1 - p_2$ $t_1 = 67$.
min. sec.	min.			
67 0	0	71·08		
69 0	2	70·70	141·77	5·24
71 0	4	70·50	141·58	5·93
73 0	6	70·15	141·23	6·48
75 0	8	69·96	141·04	7·19
78 0	11	69·66	141·73	7·74
82 0	15	69·27	140·35	8·32
86 0	19	68·96	140·03	8·95
90 0	23	68·71	139·79	9·72

The values of $t_1 - t_2/p_1 - p_2$ and $p_1 + p_2$ are plotted in figs. 1, 2 and 3. From 1 and 2 and comparison with the tables it can be seen that the limiting pressure is between 26·4 and 42·67 mm.

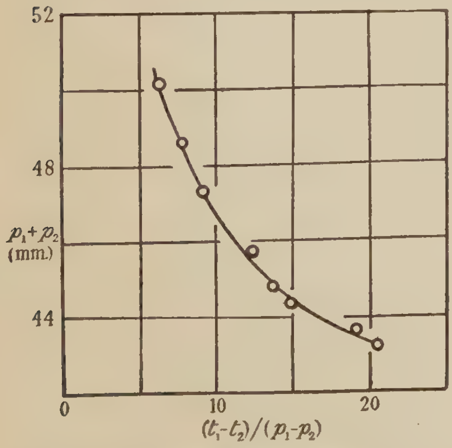

Fig. 1.—Pressure Range, 26–16 mm. Limiting Pressure greater than 26 mm.

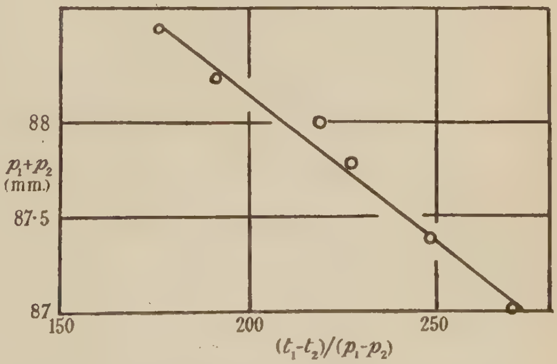

Fig. 2.—Pressure Range, 44·4–42·7 mm. Limiting Pressure less than 42·7 mm.

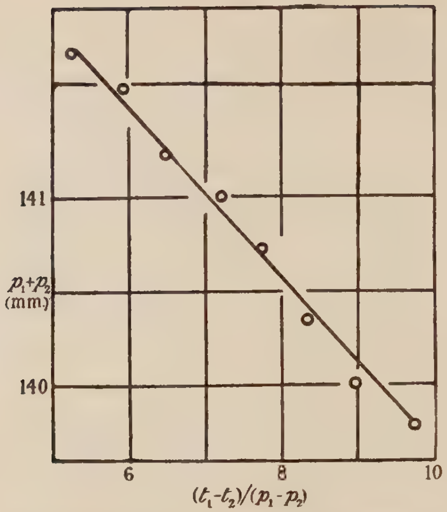

FIG. 3.—Pressure Range 71–68 mm. Limiting Pressure less than 68 mm.

The Limiting Pressure of Commercial Electrolytic Copper Foil (Inactive Copper).

Specimens of inactive copper cleaned according to the method described in Part I, were remarkably constant in their rates of oxidation. It was possible after a few trial experiments to discover the approximate position of the limiting pressure. This made possible the use of the first method. An example of a plot of equation (1) is given in fig. 4. The values of the limiting pressure found are fairly constant (see Table IV).

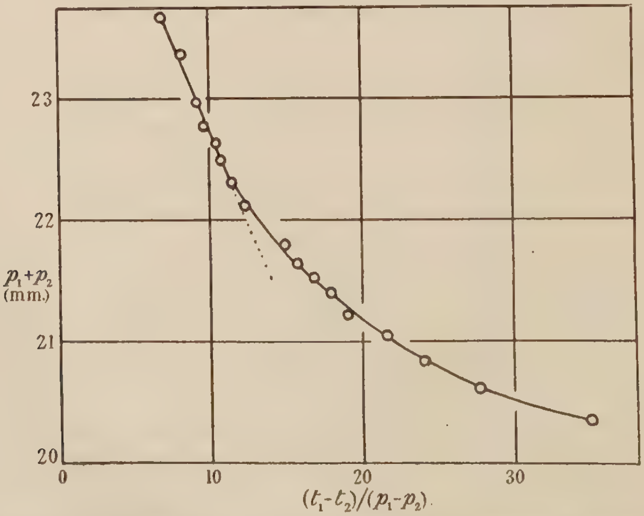

FIG. 4.—Oxidation of Commercial Electrolytic Copper Foil. Limiting Pressure = 10·3 mm.

Table IV.

Number of experiment.	Pressure range.	Limiting pressure p_L.	Time after which p_L was reached.
	mm.	mm.	min.
1	14–10	11·5	43
3	11–6·3	10·2	10
4	14–7·8	11·1	23
5	12–7·1	10·3	20
6	9·8–4	9·8	—
1*c*	18–9·5	9·5	90

The variation in the values of p_L is of the order of 2 mm. The reason for this variation, which is much greater than the experimental error, was discovered later when the influence of activation on the limiting pressure was studied. The third column of Table IV is included in order to anticipate the possible criticism that the deviations from the parabolic law are to be attributed to the sintering of the oxide layer, and that in consequence the values of the limiting pressure are spurious. An examination of the figures of this column will reveal that this criticism is not justifiable.

The results of this series of experiments also show, in accordance with those of Dunn,* that the parabolic law holds for the low temperature oxidation of commercial copper. From the figures of experiment 1*c* (*cf.* Table IV) which are plotted in fig. 5, it is clear that the parabolic law holds for periods of at least 90 minutes.

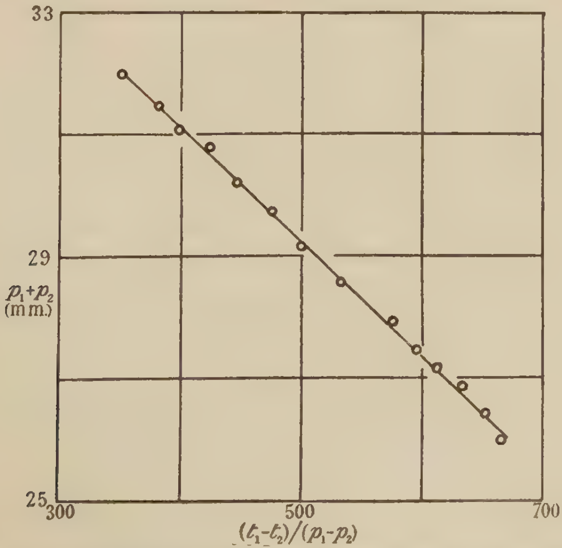

Fig. 5.—Oxidation of Commercial Electrolytic Copper Foil. Above Limiting Pressure.

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* 'Roy. Soc. Proc.,' A, vol. 111, p. 211 (1926).

The Influence of Activation on the Limiting Pressure.

A series of experiments has been carried out to determine the influence of activation on the limiting pressure. The results showed rather surprisingly that activation of the surface by alternate oxidation and reduction increased the limiting pressure. For the most part the determinations were made by the second method. Fortunately, in several cases, the limiting pressure was found to be in the range of pressures measured and it was possible to determine its value accurately.

In one series of experiments the limiting pressure of the initially inactive copper was 9·5 mm. After reduction in hydrogen at 305°, the next oxidation at 183° indicated an increased limiting pressure at 25·2 mm. The copper was now reduced and oxidised a further three times, the last reduction being carried out at 183°. This activation caused a further increase in the limiting pressure to between 50 and 60 mm. The subsequent reductions were all carried out at 183°. In the oxidation following the eighth reduction the limiting pressure was found to have reached a value of 129·3 mm. (see fig. 6). This was the highest pressure that the range of the travelling microscope would allow to be measured. This series of experiments has brought to light the remarkable fact that it is possible to increase the limiting pressure of copper by activation as much as thirteen times.

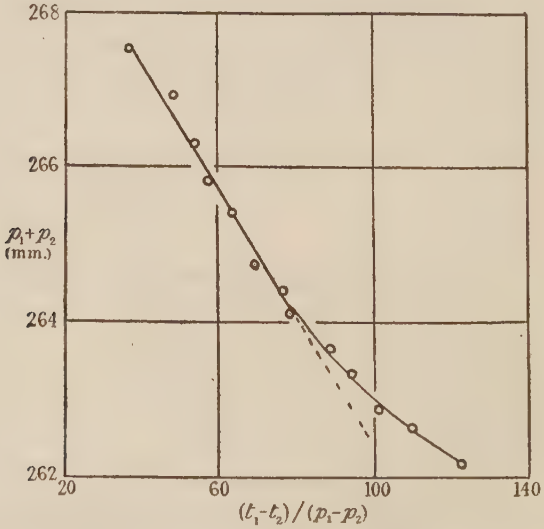

Fig. 6.—The Oxidation of Highly Activated Copper. Limiting Pressure = 129·3 mm.

The same specimen of activated copper was now sintered by heating at 305° for 2 hours. The results of the subsequent determination of the limiting pressure are those which have been used to illustrate the second method. They show that the limiting pressure has been decreased by sintering to between 26 and 43 mm. We may, therefore, conclude that while activation increases the limiting pressure, deactivation by sintering decreases it. The differences between the values of the limiting pressure noted by earlier workers are probably to be attributed to differences in the state of activation of the copper they used. The variation in the value of the limiting pressure of commercial electrolytic copper foil noticed in this work is probably due to slight differences in the state of activation of the samples.

Further measurements were made on a piece of copper which by continual oxidation and reduction had reached an approximately steady state of activation. Owing to the necessary long duration of these experiments the copper must have been poisoned, though probably only to a slight extent. The results are tabulated below.

Table V.

Number of experiment.	Pressure range.	Limiting pressure p_L.	t corresponding to p_L.
	mm.		sec.
1	100–87	89·5	265
3	98–87	89·3	173
4	98–86	90·2	266
5	106–94	95·5	215
6	103–92	92·0	300

The limiting pressure has here an approximately constant value of 90 mm.

Dunn (*loc. cit.*) has shown that the parabolic law is not obeyed for the oxidation of activated copper over the temperature range 200°–300° C. even for short periods of time. He attributed this to the rapid sintering of the oxide film. It was very necessary to show, therefore, that the deviations from the parabolic law ascribed to the limiting pressure were not due to sintering of the oxide. A comparison of columns three and four of Table V appears to show that sintering is not the cause of the deviation. It is, however, very difficult to keep activated copper in a state of constant activation during continual oxidation and reduction. To make certain, therefore, of the validity of the measurements a further test was applied. If the deviation from (1) is due to sintering, the value of p_L at which the deviation occurs should depend upon the value of t_1 chosen. Plots of (1) were therefore made using different values of

t_1. In no case was the limiting pressure found to be dependent upon the value of t_1.

We may, therefore, conclude not only that the earlier statements made concerning the influence of activation on the limiting pressure are valid, but also that the parabolic law is obeyed at 183° with activated copper over considerable ranges of time. For example, in the case of the most active copper the limiting pressure was reached only after 481 seconds. As a further example, in fig. 7, equation (1) is plotted for the oxidation of a moderately activated sample of copper. The equation held throughout the whole time of oxidation, which was 24 minutes. These results are not necessarily in disagreement with those of Dunn for the increase in the rate of sintering between 183° and 209° may well be considerable.

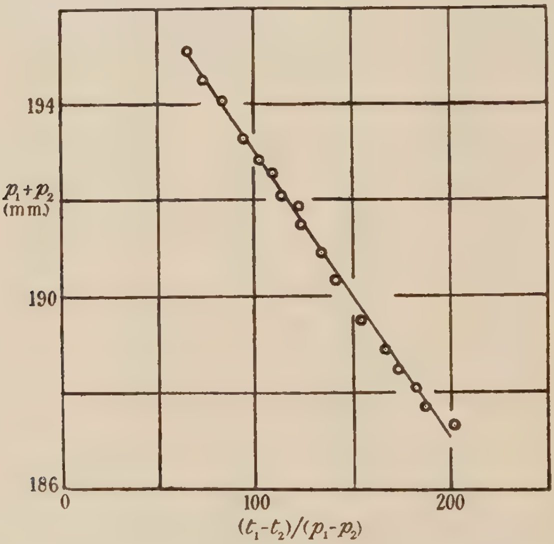

Fig. 7.—Oxidation of Activated Copper at 183° C. Above Limiting Pressure.

The Theoretical Significance of the Limiting Pressure in its Relation to Activation.

From evidence brought forward in Part I it was demonstrated that adsorption is a necessary preliminary to diffusion. Further, it was suggested that oxygen diffused through the cuprous oxide only along the grain boundaries. In an attempt to explain the limiting pressure phenomena, it is a natural extension of these ideas to assume that at pressures below the limiting, the grain boundaries in the surface are no longer saturated with adsorbed oxygen. The first attempt to develop the influence of activation and limiting pressure, using the method of Langmuir* to obtain the relationship between the amount adsorbed and the pressure, was unsuccessful.

Consider unit area of surface and let ϕ be the fraction of that area covered by grain boundaries. Then if θ is the fraction of ϕ covered with adsorbed oxygen, the rate of condensation at pressure p is

$$kfp\phi(1-\theta), \tag{2}$$

where f is the accommodation coefficient and k a constant. The rate of evaporation consists of two terms, one due to the evaporation into the gas phase, and the other to the evaporation into the oxide. Let ν_g and ν_s respectively be the rates of these processes from unit area of grain boundary. Then, the total rate of evaporation from an area θ of grain boundary is

$$(\nu_g+\nu_s)\,\theta\phi. \tag{3}$$

Since under the conditions of these experiments an adsorption equilibrium always exists, we may equate (2) and (3)

$$kfp\phi(1-\theta)=(\nu_g+\nu_s)\,\theta\phi$$

$$p=\frac{(\nu_g+\nu_s)\theta}{kf(1-\theta)}.$$

Complete saturation occurs theoretically when $\theta=1$ or when p is infinite. Experimentally this condition does not arise since θ approaches unity asymptotically as p increases.

The limiting pressure is, therefore, that pressure at which the difference between θ and unity begins to be large enough to have an appreciable effect upon the rate of oxidation. This pressure will be finite and we may write for it

$$p_{\mathrm{L}}=\frac{(\nu_g+\nu_s)\,\theta}{fk(1-\theta)}.$$

Activation of a surface should not alter any of the factors of this equation. One would, therefore, expect from the application of Langmuir's treatment of the gas/solid interface to the problem that activation would not increase the limiting pressure.

The solution of the difficulty is obtained if we no longer make Langmuir's assumption of a stationary adsorbed molecule. The lateral diffusion of oxygen adsorbed on cuprous oxide has already been suggested by the results of the oxidation at low pressures. Under the conditions of lateral diffusion we may

* 'J. Amer. Chem. Soc.,' vol. 40, p. 1361 (1918).

no longer consider only the equilibrium between the gas phase and the grain boundaries. We have to consider the equilibrium between the *whole* surface and the gas phase.

The rate of condensation on to unit area of cuprous oxide is

$$fkp\,(1-\theta), \tag{4}$$

where θ is the fraction of surface covered.

The rate of evaporation will be formally the same as before

$$(\nu_s+\nu_g)\,\theta. \tag{3}$$

It will be more satisfactory, however, to include a term to account for the evaporation of adsorbed molecules owing to collision with molecules from the gas phase incident on the surface. This may well become the chief term at high pressures. We have, then,

$$(\nu_s+\nu_g)\,\theta+\nu p\theta. \tag{3A}$$

Equating

$$fkp\,(1-\theta)=(\nu_s+\nu_g)\,\theta+\nu p\theta,$$

and we may write for the limiting pressure

$$p_{\mathrm{L}}=\frac{(\nu_s+\nu_g)\,\theta}{fk\,(1-\theta)-\nu\theta}. \tag{5}$$

The only factor on the right-hand side of this equation which can be altered by activation is ν_s. The rate of evaporation into the cuprous oxide, ν_s, refers now not to the rate of evaporation from unit area of grain boundary but to the rate of evaporation from unit area of the whole surface. This is obviously dependent upon the number of grain boundaries in unit area of the surface. Since this number increases with activation, ν_s must increase. Therefore, as (5) shows, p_{L} must also increase with activation.

The point may be made clearer still by the use of an analogy. Consider a vessel with a very finely perforated bottom into which water is being poured. In order to keep the bottom covered, water will have to be poured in at a definite rate which will correspond with a given pressure head. If now the number of perforations is increased then the rate at which water will need to be poured in to keep the bottom covered will have to be increased. Activation is analogous to increasing the number of perforations in the bottom of the vessel. The increase in the limiting pressure is the analogue of the increase in the pressure head.

These results appear, therefore, to provide definite evidence of the lateral diffusion of oxygen adsorbed on cuprous oxide at 183°.

Summary.

The limiting pressure below which the oxidation of copper ceases to follow the parabolic law is the higher the more active the copper is. For commercial electrolytic copper foil this limiting pressure is about 10 mm. By activation of the copper it was possible to increase the limiting pressure as much as thirteen times. Further, sintering of the surface decreased the limiting pressure.

It is suggested that at the limiting pressure the grain boundaries in the surface of the cuprous oxide are just saturated with adsorbed oxygen. On this basis it is shown that the influence of activation on the limiting pressure is accounted for if it is assumed that the oxygen adsorbed on cuprous oxide at 183° C. is able to diffuse laterally.

Dunn's observation that the oxidation of commercial copper at low temperatures follows the parabolic law is confirmed. It has also been found that the parabolic law describes the oxidation of activated copper at 183° over relatively long periods of time provided that the oxygen pressure is high enough.

In conclusion, I should like to express my thanks to Dr. E. K. Rideal for his continued interest and advice during the course of this research, and to Prof. T. M. Lowry for much useful criticism. My thanks are also due to the British Non-Ferrous Metals Research Association for a grant.

Cleavage Tests of Timber.

By Prof. E. G. Coker, F.R.S., and Mr. G. P. Coleman, B.Sc., University College, London.

(Received May 21, 1930.)

The value of physical tests of the properties of most materials, prior to their use for construction and like purposes, is now so well established, that such tests are carried out as a matter of ordinary routine.

Many of these, although apparently simple, prove, on detailed examination, to be much more complex than is apparent at a first glance, as for example various tests of hardness, which are extremely useful in practice, although their accurate scientific interpretation is still in an unsatisfactory state.

This also appears to be the case with tests of timber, which is probably still the most valuable of all materials in general use, on account of the vast available supplies distributed widely over the earth's surface, affording a range of physical properties adapted to the most diverse needs, while stocks are capable of replenishment indefinitely with scientific management.

Most of the early experimental information on timber relates to its strength in large baulks, such as are required for engineering structures, where weight is not usually an important factor, but the application of timber to aeroplane construction, where weight is of prime importance, had led to an extensive re-examination of its mechanical and other properties for aeronautical uses.

An account of some of these researches during the war period is given by Jenkin* where, among other matters, the nine primary physical constants of St. Venant's theory† are determined for several timbers used in aeroplanes. Another theory, with 12 primary constants, has been proposed recently by Price‡ in order to obtain more accurate agreement with the experimental facts which are not in complete accord with the older theory.

Thus in practical applications the anisotropic character of timber calls for special experimental tests of its properties, in addition to those usual for materials of an approximately isotropic character, and one of these is the determination of its resistance to cleavage. This is usually determined by applying equal and opposite loads, up to fracture, along the diameters of incomplete holes bored in flat specimens of timber, cut in such a manner that the stress in the material is normal to the direction of the grain. Such tests are in fact carried out in many timber testing laboratories, and are capable of giving comparative information, as between various timbers, without, however, affording any precise data as to the stress at which any specimen begins to cleave.

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* "Report on the Materials of Construction used in Aircraft and Aircraft Engines," H.M. Stationery Office.

† Todhunter and Pearson, "History of Elasticity," 198, 282, 308–313.

‡ "A Mathematical Discussion on the Structure of Wood in Relation to its Elastic Properties," 'Phil. Trans.,' A, vol. 228, p. 1 (1928).

At the suggestion of Sir Alfred Ewing, K.C.B., F.R.S., this matter has been examined by photo-elastic means with isotropic material.

It will be useful, therefore, to mention here some advantages, and also some defects, of this method of analysis as applied to this type of problem.

An obvious defect is that the stress distribution in an isotropic body cannot be the same as in an anisotropic one. Although this is so, yet it is found that some peculiarities of the behaviour of timber under cleavage tests, and hitherto unexplained, can be accounted for, as will appear later.

A satisfactory feature of this analysis is that, in the tests to be considered, the specimens are plates with single boundaries, and it is known, under such conditions, that plane stress distributions in isotropic bodies, under the same conditions of shape and loading, are independent of the physical constants of the materials.

It is, however, to be remarked that in the usual cleavage tests of timber, plates of considerable thickness are used, so that plane stress conditions are probably only realised approximately.

Another matter, worthy of mention, is that in properly seasoned timbers, the stress distributions up to fracture are of the elastic type, and therefore if a distribution is known for any load, it is only a matter of simple proportion to find the stress for any other possible load. Hence, subject to the limitations described, any elastic distribution found in a model, may be used for comparison with its timber proto-type at any stage of the loading.

It will be convenient to examine first, the nature of the stress distribution in a cleavage test piece, when there is only one incomplete hole to which load is applied, as the more complex case, with two such holes, forms a natural sequence to this elementary form.

Such a specimen is shown in the accompanying fig. 1, in the form of a model of a test-piece $3\frac{3}{4}$ inches long, 2 inches deep and 2 inches thick, with an incomplete hole in it, 1 inch in diameter, struck from a centre on the main horizontal axis and $\frac{1}{4}$ inch from the left-hand end.

This is shown, when strained by the rounded edge of a disc A thrust in edgeways. The red isochromatic bands, marked on this figure, are those revealed in circularly polarised light, with the order of each band marked against it. The principal feature of interest here is the arrangement of the bands, of order 2, with reference to the circular contour. These indicate that the maximum stresses on this contour are at a considerable angular distance from the central line, while the disposition of other bands at the contact areas, and along the horizontal sides, show that stresses of considerable intensity exist at these places.

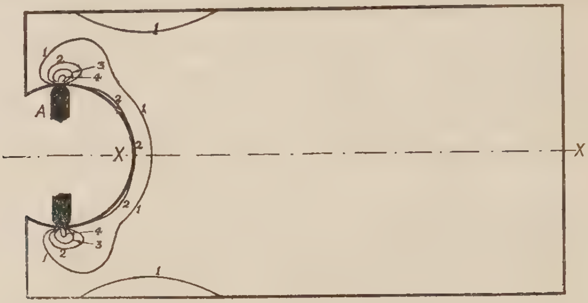

Fig. 1.—Red Isochromatic-Bands in Cleavage Test Specimen.

The contact stresses at the circular boundary, due to the applied loads, are of no practical significance here, and have not, therefore, been measured. On the remainder of the circular arc the stress intensities are of importance, since the way the specimen will fracture depends on these latter stresses.

As will be seen from fig. 2, a load of 35 lb. causes a stress of 1316 lb. per square inch at the end A of the central line, and along the circular arc, until near the contact points, this is the smallest stress on this contour. The maximum stresses are at points B_1 and B_2 at angular distances of 50°, and of an intensity of 1670 lb. per square inch or 26·9 per cent. greater than at A. These maxima stresses are, however, inclined to the direction of the grain of the timber, which, in these tests, is chosen to run parallel with the axial line. The normal stresses across the grain at B_1 and B_2 are therefore $p \cos^2 \theta$, where $p = 1670$ and $\theta = 50°$. The normal stresses, so calculated at every point, give the dotted curve drawn in this figure, from which it will be observed that a maximum value for this normal component is reached at angular distance of 10° from the central line, with intensities of 1329 lb. per square inch.

If the material fails owing to this stress across the grain, then with isotropic conditions it will fail at the points C_1 and C_2 instead of at A. This latter type of fracture happens sometimes in such test members, and having regard to the nature of the distribution along this contour it is not difficult to understand the reason for failures at places other than the central cross section.

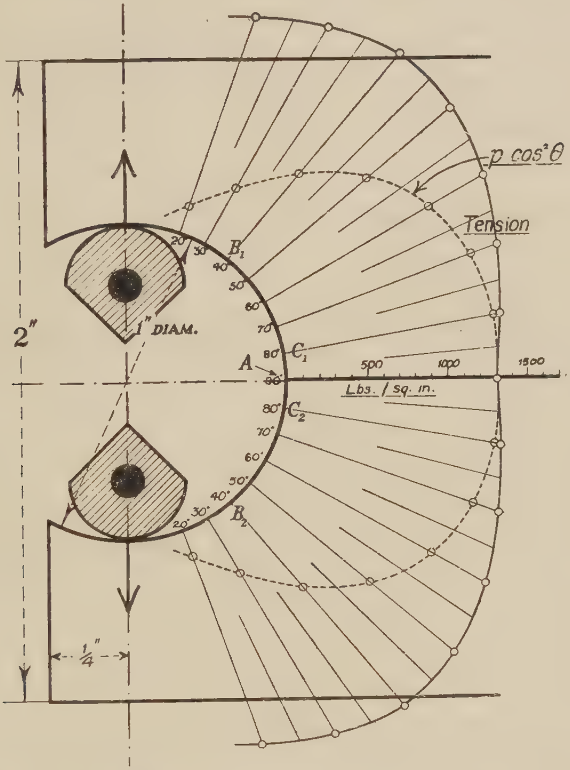

FIG. 2.—Stress at Hole Contour. Load applied, 35 lb. Thickness of Nitro-cellulose, 0·184 inch.

Evidently failure will also depend on the special characteristics of the anisotropy, and if this is of such a kind that the timber is naturally weak at A and strong at C_1 and C_2, then failure may commence at A, even although the normal stress across the grain there is lower than C_1 and C_2, whereas for equality of physical conditions it must occur at these latter places if intensity of normal stress across the grain is the criterion of failure.

This remark also illustrates the difficulty of obtaining precise data of cleavage property, unless the circumstances of the test can be so arranged that the conditions at the section where facture takes place are similar to those of other timbers to be compared by this test.

The nature of the distribution of the stress along the central section is also of interest, since it suggests that the shape of the test member is a wasteful one.

As will be seen from fig. 3, the normal principal stress P at the circular contour, falls very rapidly, as the central cross section is traversed from left to right, and it ultimately changes sign and becomes a feeble compression stress before it finally vanishes well within the length of the member. Accompanying this is a minor principal stress Q along the section, which is always tensional, with a maximum value of 340 lb. per square inch at a distance of 0·5 inch from the curved contour.

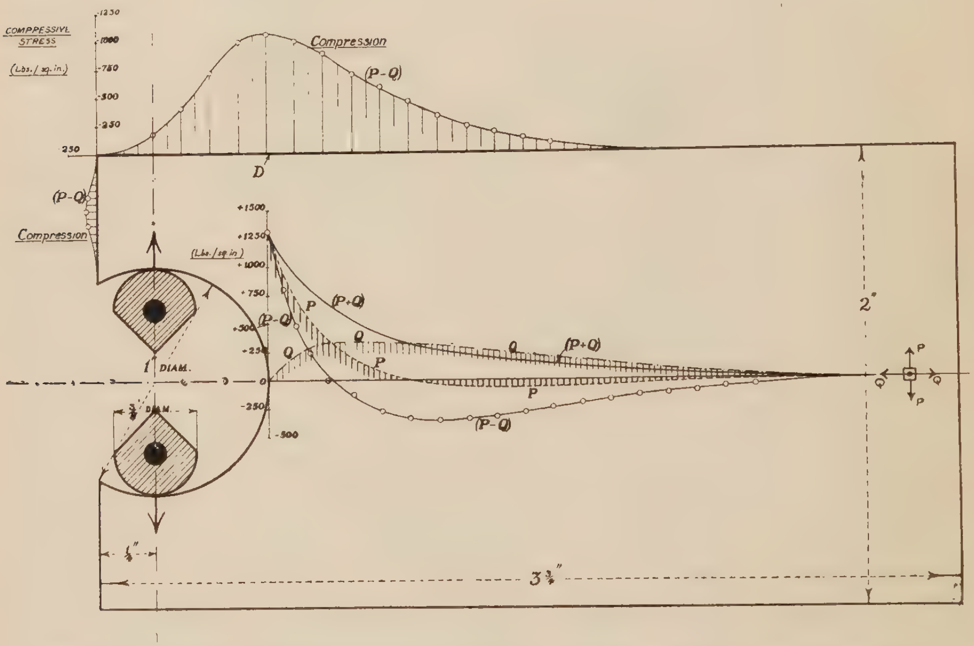

FIG. 3.—Thickness of Nitro-cellulose, 0·184 inch. Load applied, 35 lb. Stress distribution at the central cross section (see fig. 8).

These and other stresses are found in the usual manner by observations of the sums and differences of the principal stresses at various points, as indicated in this diagram, but it is not necessary to describe the details of the measurements here, as the processes can be assumed to be well known.*

It is evident from these results that the right-hand end of the test piece is never under any stress before fracture commences, and it is, therefore, useful to ascertain the effect of reducing this dimension. This is examined by removing, in succession, rectangular strips from the right-hand end, each half an inch in width, until some change in the distribution at the other end becomes noticeable. The effects of these removals of material can be easily watched along the central axis, and also along the upper and lower sides, which latter are highly stressed near the circular contour, with a maximum stress in compression of 1050 lb. per square inch at points D, $\frac{3}{4}$ inch from the left-hand end of this edge. As may be anticipated from the P and Q curves of stress distribution shown in fig. 3, the effect of cutting off two or three such strips in succession is so small as to produce hardly any change of stress distribution in the rest of the specimen, and it is only after the fourth cut, when the distance of the new vertical edge is 2 inches from the line of load, that changes occur of any importance.

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* The methods and apparatus used are described in the following papers: "Stress Distributions in Engineering Materials," B.A. Report, 1914; "Polarised Light and its Applications," 'Proceedings of The Royal Institution,' 1916; "Contact Pressures and Stresses" and "Elasticity and Plasticity," 'Minutes of The Proceedings of the Institution of Mechanical Engineers,' 1921 and 1926; "Photo-Elastic Measurements of Stress Distribution," 'Cantor Lectures, Royal Society of Arts,' 1927.

As is also evident from fig. 3, the stress which will be found along this newly-formed contour is a variable compression stress, which from symmetrical considerations must have a maximum value at its central point, as shown in fig. 4, accompanied by relatively small changes in the stress distributions along the other contours.

The removal of a further strip, $\frac{1}{2}$ inch in width, modifies the whole stress distribution greatly, and, as will be seen from fig. 4, the maximum stress along the new vertical edge is increased to 686 lb. per square inch, while the character of the distribution round the circular contour also undergoes a marked change, for whereas in the original member the maximum stresses of 1670 lb. per square inch were at angular distances of 50°, which subsequent cuts have not altered very much, we now have a maximum stress at the centre of 1980 lb. per square inch, which diminishes with angular distance so very slowly, that at 50° it is only 48 lb. per square inch less than the central value. The effect of this last change ensures maximum stress conditions at the central section, and the operation of the $\cos^2 \theta$ law of normal distribution ensures that fracture will take place centrally, unless the anisotropic conditions are especially unfavourable.

The stress along the central line of this altered form is of some interest, and the distribution is shown in fig. 5, from which it appears that for a load of 30 lb. on a plate 0·202 inch thick, the maximum tensional stress P of 1980 lb. per square inch falls rapidly in value, and passes through zero at about the centre of the section, with a final value, in compression, at the outer extremity of 686 lb. per square inch. This is accompanied by a cross stress Q, which is

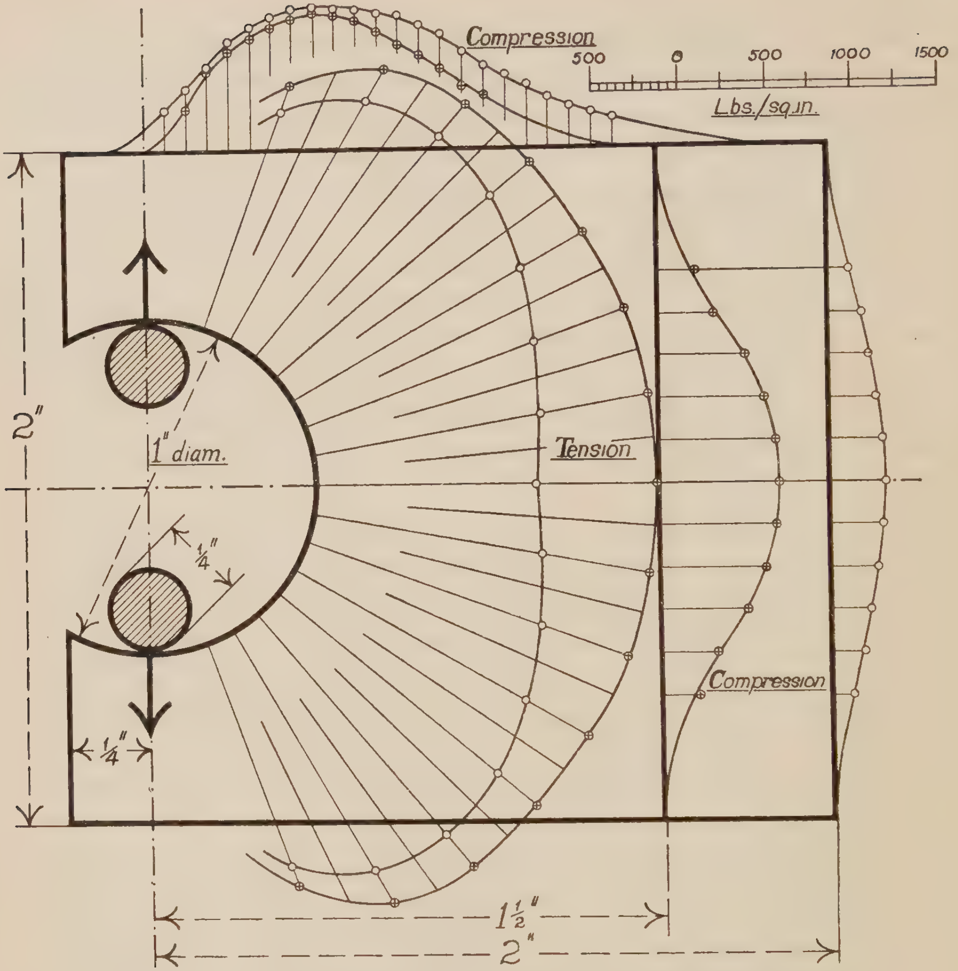
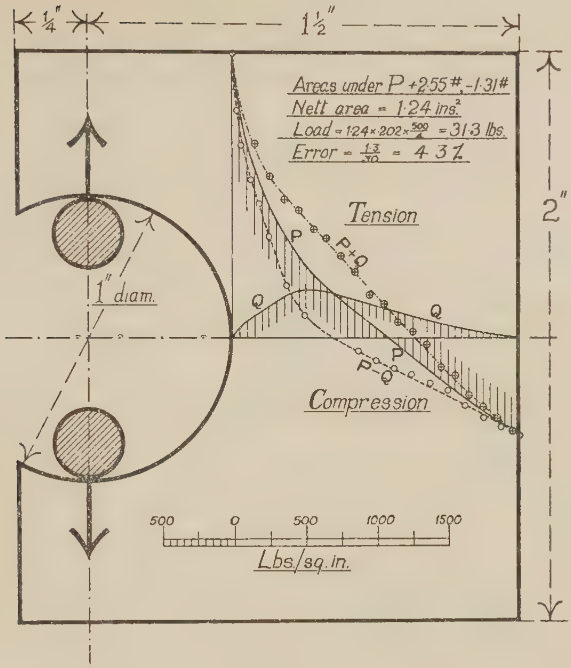


Fig. 4.—Contour stress distributions. Thickness of nitro-cellulose, 0·202 inch. Load, 30 lb.

always tensional, with a maximum value of 335 lb. per square inch at a distance of ¼ inch from the left-hand end. The details of the measurements are shown in Table I and a graphical integration of the area bounded by the P curve, the cross section and the end ordinates, shows that the load is slightly over-accounted for to the extent of 4·3 per cent., a result probably due to small errors in the measurements of (P + Q), the curve of which, as will be seen, shows a slight bulge near its centre, which is otherwise difficult to understand. As the general features of the distribution are clear enough, it is probably not necessary to re-determine this stress curve more accurately. The main effect



¼"
1½"
2"
Areas under P +2·55#, -1·31#
Nett area = 1·24 ins²
Load = 1·24×·202×500/4 = 31·3 lbs.
Error = 1·3/30 = 4 3 %
Tension
Compression
1" diam.
P
Q
P×Q
500
0
500
1000
1500
Lbs./sq. in.

Fig. 5.—Stress distribution at the central cross-section. Thickness of Nitro-cellulose, 0·202 inch. Load applied, 30 lb.

Table I.—Stress Distribution along the Central Section of fig. 5.

Distance from left-hand end (inches)	0	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{3}{8}$	$\frac{1}{2}$	$\frac{5}{8}$	$\frac{3}{4}$	$\frac{7}{8}$	1
Stress P in lb. per square inch	1980	900	500	260	57	−135	−333	−510	−686
Stress Q in lb. per square inch	0	215	335	295	223	150	80	35	0

of this diminution in length is to produce a much more satisfactory distribution along the circular contour where it is desired that fracture shall commence.

The same type of change can also be produced in other ways, as for example by increasing the height of the specimen, as is shown in fig. 6, where the effects produced by successive additions of $\frac{3}{4}$ inch to this dimension are traced, and the general result is seen to be that all stresses diminish with an increase of this dimension. Features of special importance are the changes in the polar curves of stress at the circular contour, which contract in size, and tend to a maximum value at the central point and actually show this feature at depths of 3½ inches or more, although for this particular depth (curve No. 3) the diminution of stress with angular distance is very small, amounting to only 22 lb. per square inch at 30° on each side. The details of the measurements for this contour, due to variations in the depth of the specimen, are shown in the accompanying Table II, the central section being taken as 90° to agree with fig. 6.

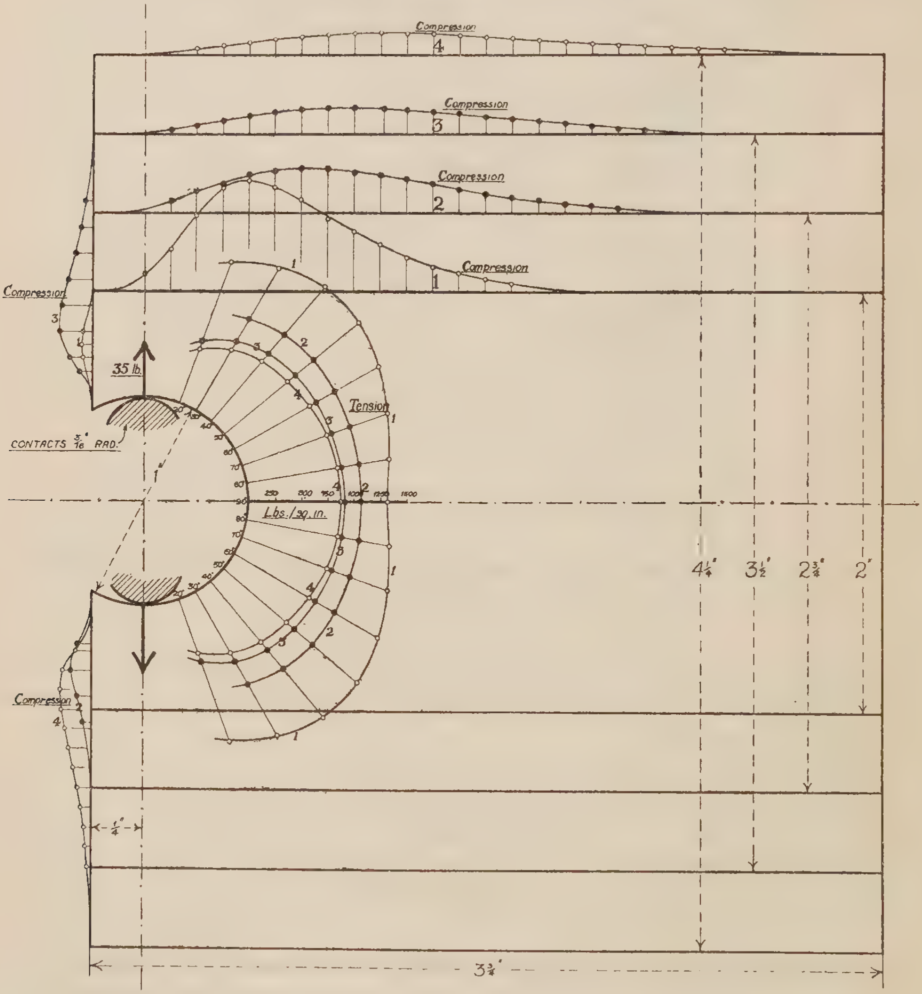


Fig. 6.—Contour Stresses in specimens of different heights. All Stresses are for a 35-lb. load. Tensile stress plotted inward from edge. Compression Stress plotted outward from edge.

Another way of producing the same desirable feature in the stress distribution

Table II.

Angle from vertical.	Stresses in lb. per square inch for a height of specimen in inches.			
	2.	2¾.	3½.	4¼.
°				
20	1425	—	619	535
30	1560	1002	750	660
40	1670	1070	836	738
50	1659	1103	872	778
60	1575	1093	885	816
70	1466	1084	894	849
80	1370	1080	903	864
90	1315	1065	907	870

round the circular contour, is to diminish the radius of this latter, but this change naturally has a very limited scope owing to the necessity of accommodating the loading shackles within this contour.

An examination of this first form of cleavage test member, and the variations of stress distribution in it produced by changes in dimensions, enable us in some measure to forecast the general type of effect which will be produced when the loading conditions are duplicated on a member suitably modified. A standard test member, of the kind now used in timber testing laboratories, is constructed by boring two 1-inch holes, with centres 2 inches apart, in a rectangular block of timber 2½ inches long, 2 inches deep and 2 inches thick, so as to leave a central cross section of 1 inch width symmetrically disposed between the holes, as shown in fig. 7.

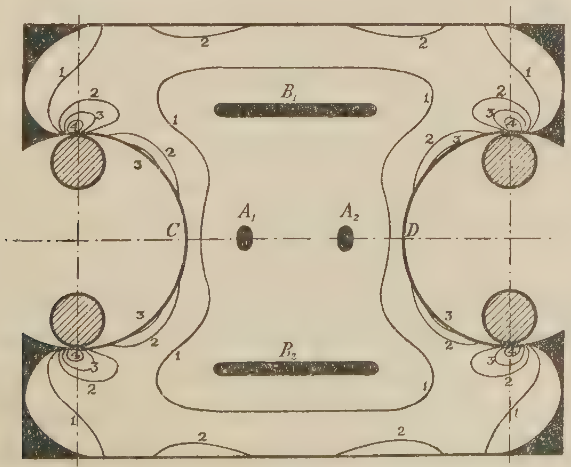


FIG. 7.—Distribution of Isochromatic Bands in Cleavage Test Specimen.

As before the grain of the timber is arranged to run parallel to this main cross section, and equal loads are now applied along the diameters of these broken holes in directions perpendicular to this section.

An examination of such a form in circularly polarised light shows an interesting distribution, which although more complicated than before, presents anew some features already made familiar by a study of the earlier case, with some additional ones due to the duplication.

Some of these features are apparent at once, from the isochromatic bands shown in fig. 7, which indicate, by closely lying bands of the second and third orders, well marked features of maximum stress intensity at the circular contours at considerable angular distances from the central cross section These stresses are accompanied by variable stress distributions, with considerable maximum intensities, along the horizontal sides, and small stresses along the verticals. New features are the presence of stress difference zeroes A_1 and A_2 symmetrically arranged along the central line, and straight bands B_1 and B_2 of the same kind parallel to the central axis. These latter bands suggest that possibly the member may be considered as a pair of double cantilever beams of somewhat peculiar shape joined together at a centrally supporting base CD, and loaded at their outer extremities. This in fact gives an elementary idea of the nature of the stress distribution, which further photo-elastic analysis reveals.

The stresses round the circular contours, fig. 8, show that maximum intensities of 1876 lb. per square inch are reached at angular distances of 50 from the axial line, where a stress of 765 lb. per square inch is found, when a total load of 80 lb. is applied to a plate 0·197 inch thick. This distribution gives a maximum normal stress across the grain of 1060 lb. per square inch at angular distances of 45°, so that the form of this specimen is not conducive to fracture along the central cross section. This effect may, possibly, be increased when the load is distributed over arcs of the contour by grips of the same curvature, since the effect of this is, in general, to produce a higher contact pressure at the end points of the arcs than at any other place. Some cleavage test specimens are, in fact, found to fail at an inner end point of contact. The compression stresses along the upper and lower edges are also large, with maximum intensities of 1083 lb. per square inch at two points, separated by a central minimum stress of 971 lb. per square inch.

The presence of two stress difference zeroes, in fig. 7, on the central cross section, not very distant from their respective circular contours indicate that a cross stress Q, of considerable magnitude, may be expected, and this is borne

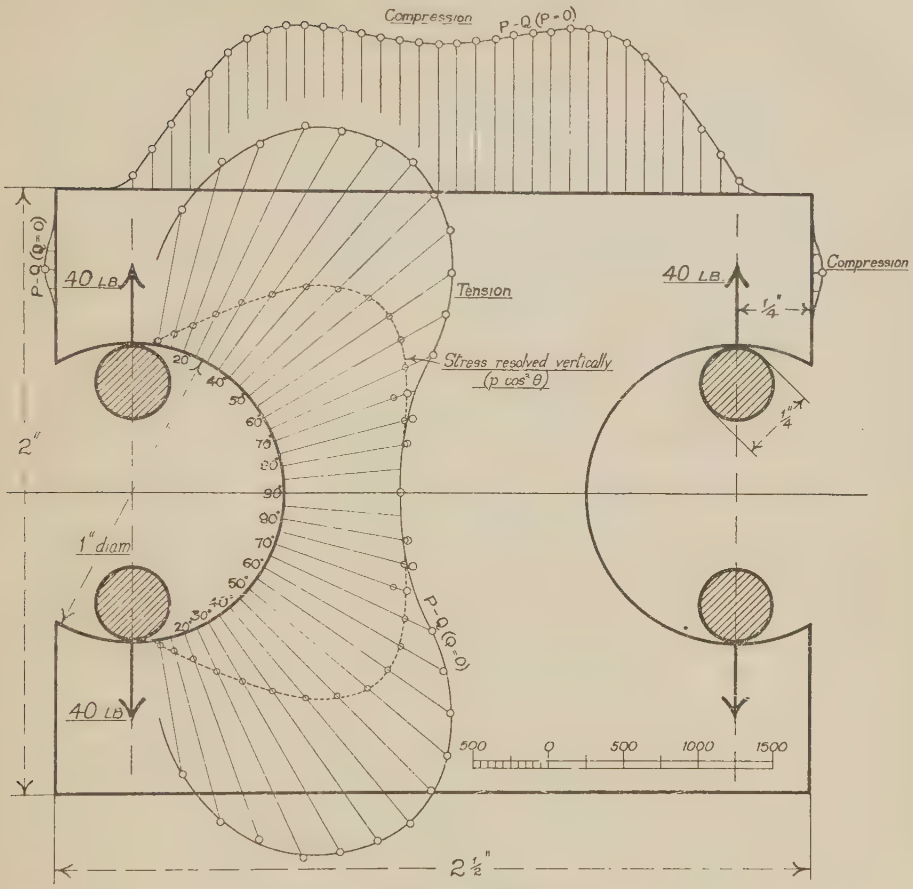

Compression
P-Q (P=0)
P-Q (Q=0)
40 LB.
Tension
Compression
40 LB.
$\frac{1}{4}$"
Stress resolved vertically
(p cos² θ)
$\frac{1}{4}$"
2"
20
40
50
60
70
80
90
90
80
70
60
50
40
30
20
1" diam
P-Q (Q=0)
40 LB.
500
0
500
1000
1500
2½"

FIG. 8.—Contour Stress distribution.

out by the stress exploration along this line, and shown in fig. 9, in which Q is shown to rise to a central tensional value of 660 lb. per square inch, while the normal stress P at the same point reaches the low value of 250 lb. per square inch, with end maximum values of 765 lb. per square inch, or not a great deal more than the maximum value of Q. The state of stress along the section, at which the member is designed to fracture, is, therefore, very different from the earlier case, while the stresses at the circular end contours are very unfavourable for this purpose, as already described. There is in fact no real basis for a comparison of results on these two forms.

An integration of the area under the P stress curve shows that the whole of the load is accounted for to within 2·25 per cent. in this case also in excess.

It is of interest to examine here the suggestion that this specimen may be

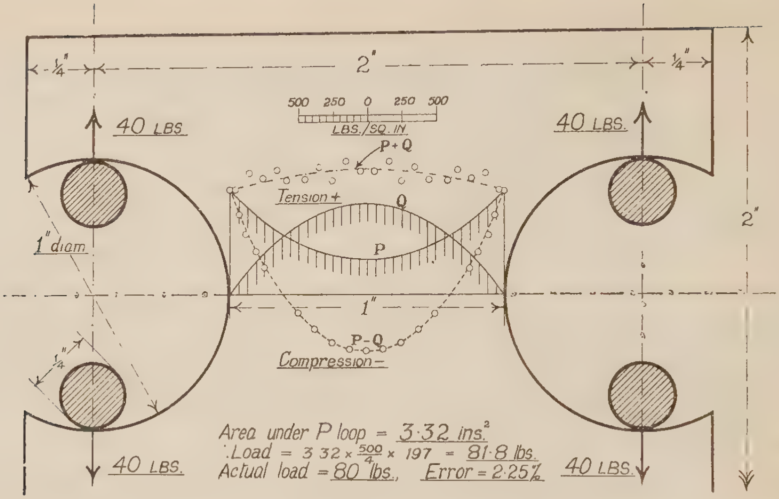

¼"
2"
¼"
500 250 0 250 500
LBS./SQ. IN.
40 LBS.
40 LBS.
P+Q
Tension +
Q
P
1" diam.
1"
2"
P-Q
Compression –
¼"
Area under P loop = 3·32 ins.²
∴ Load = 3·32 × 500/4 × ·197 = 81·8 lbs.
Actual load = 80 lbs., Error = 2·25%
40 LBS.
40 LBS.

Fig. 9.—Stress distribution at the central horizontal cross section. Thickness of nitro-cellulose, 0·197 inch.

regarded as a pair of double cantilevers joined together, and the imperfection of the analogy is shown at once by the stress system of fig. 10, where the stress

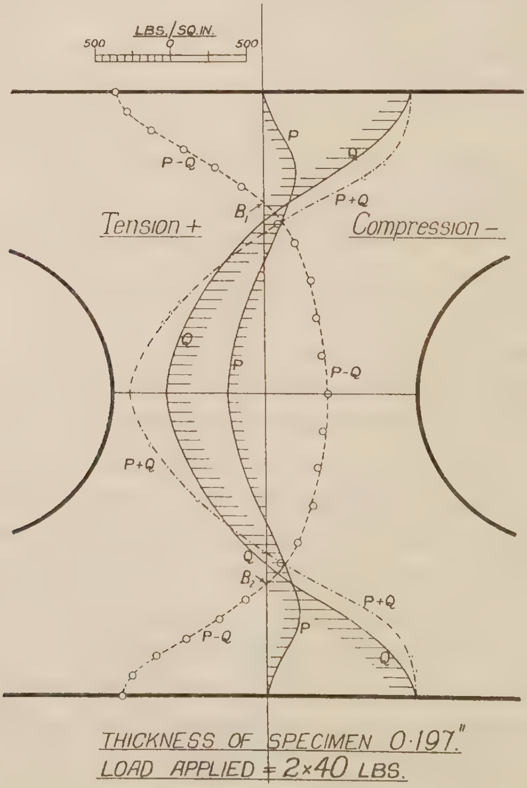

LBS./SQ.IN.
500 0 500
P
Q
P-Q
P+Q
B₁
Tension +
Compression –
Q
P
P-Q
P+Q
Q
B₂
P+Q
P
P-Q
Q
THICKNESS OF SPECIMEN 0·197"
LOAD APPLIED = 2×40 LBS.

Fig 10.—Stress distribution at the central vertical cross section.

Q normal to the perpendicular cross section is seen to be non-linear throughout, while the principal stress P at right angles is also non-linear and cuts the Q system at two points A_1 and A_2 which lie on their respective stress difference zero lines, showing that these latter are not neutral axes. Both stress systems show no resultant force when integrated over the section.

Variations of this standard form have also been examined by diminishing the radii of the holes and the width in such a manner as to still keep the central cross section of the same dimensions. It is probably sufficient here to state the results obtained in general terms. It is found that the first change does not improve the distributions at the circular contours very much, although the cross stress Q along the cross section is diminished relatively to the normal stress P.

This new form, when altered further by increasing the depth, shows an appreciable improvement in the distribution at the circular contours at the expense of a relative rise in the cross stress Q in relation to the normal stress P.

Each form of isotropic test piece is therefore shown to give rise to a stress distribution peculiar to itself, and if anisotropy is brought into account, it can only be safe to assume that it adds to the complication of these isotropic stress conditions.

It may be inferred, therefore, that fair comparable results in cleavage tests of these types can only be expected when one form is adhered to, and that a numerical value of cleavage property, calculated from the known load at fracture, and the assumption of stress conditions found from isotropic models, can, at best, only afford an approximate numerical value of this property, with either of these two typical forms, or any variations of them due to relative changes of dimensions.

Owing to the complicated character of the stress distributions shown by this investigation, it is suggested that, probably, it would be better to rely on a simple tension test to define cleavage property arranged in such a manner that load is applied uniformly and normally to the grain of the timber. Such a test would, in a short length, exert normal tension across a large number of cells, and its selective action would ensure fracture at the weakest place. Specimens of this type, of circular cross section, and turned down to a small diameter at the central part, have been shown* to fracture across the grain. The numerical value of the stress required to effect this would tend to give a minimum value of the cleavage property when defined in this manner.

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* Jenkin, *loc. cit.*, p. 98.

Experiments on the Exchange of Energy between Gas, Solid, and Adsorbed Layer in vacuo.—I. *A Method of Detecting Variations in the Thermal Efficiency of Molecular Collisions.*

By M. C. Johnson, M.A., M.Sc., Lecturer in Physics, Birmingham University.

(Communicated by S. W. J. Smith, F.R.S.—Received March 29, 1930.)

1. *Introduction.*—Following Knudsen and Smoluchowski, the thermal efficiency of encounters between the molecules of a rarefied gas and of a solid surface may be characterised by the "accommodation coefficient,"

$$\alpha = \frac{T_1 - T_2}{T_1 - T_2'},$$

where T_1 is the temperature corresponding to the energy of a gas molecule approaching the solid surface, T_2 the temperature on leaving the surface, and T_2' the temperature of the molecules which constitute the surface layer. The value of α has been measured in certain cases,* and is generally considered to depend on the physical condition of any given surface; for instance, Langmuir has given reasons for expecting α at a clean metal wire not to be the same as when the metal carries adsorbed vapour, while Hughes and Bevan† have shown that α for H_2 on nickel can be increased from 0·25 to 0·48 by oxidation.

Since Langmuir‡ has shown that a connection exists between the time taken for gas molecules to reach thermal equilibrium with a surface and the probability of their condensing thereon, variations in α, for different surface conditions of any given solid in any given gas, are of importance to the physics of adsorption. Since differences in thermal exchange at a bare lattice and at an adsorbed layer will share largely in determining whether the latter is monomolecular or multimolecular in structure, these differences are among the data preliminary to a physics of heterogeneous chemical reaction, in so far as this depends on the structure of the interfacial layer.

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* Knudsen, 'Ann. Physik,' vol. 34, p. 593 (1911); Soddy and Berry, 'Roy. Soc. Proc.,' A, vol. 84, p. 576 (1911).

† 'Roy. Soc. Proc.,' A, vol. 117, p. 101 (1927).

‡ 'Phys. Rev.,' vol. 8, p. 149 (1916).

The chief difficulty in the interpretation of variations in α is the isolation of a changing state of surface from other variables ; in the present paper, which is concerned with variations and not with absolute values, an experimental arrangement is described which is sensitive to small changes in α for hydrogen at the glass surface of a vacuum apparatus, other conditions being constant to a specified degree of approximation.

The method is applied here to tracing a 20 per cent. change in a certain function of α as the surface is progressively freed from adsorbed vapour, and it is hoped to discuss later the treatment of the solid with artificially deposited gas layers.

2. *Principle of Method.*—An electrically-heated wire in an enclosure of fixed dimensions loses energy at a rate proportional to the surrounding gas pressure if two conditions are obeyed, firstly, that the molecular free path is not small compared with the enclosure, and, secondly, that there is still sufficient residual gas for cooling to be mainly due to its conduction. In most gases and apparatus of ordinary dimensions these are fulfilled between, say, 1/20 and 1/10,000 mm. pressure. If the pressure is changed, the accompanying response of the temperature and resistance of the wire constitutes the basis of the vacuum gauges of Pirani, Hale, and Campbell. It is well known that the time lag in this response may be of the order of a minute or two, the attainment of thermal equilibrium occupying a considerable time at low pressure. Now the time taken to establish by conduction a given temperature gradient between wire, low pressure gas, and wall of vessel, must depend, other things being equal, on the efficiency of the collisions between gas molecules and wire and gas molecules and wall, for it is by these collisions that energy is transferred from the one solid to the other. Hence a method of investigating α at wire and wall might be expected to evolve from measurements of the rate of electrical response of a wire to pressure changes in a surrounding vacuum.

In practice, the direct observation of rates of response was found not to be an accurate means of tracing changes in surface condition ; greater sensitivity, reproducibility, ease and rapidity of detection, were obtained when the following differential method was adopted, *i.e.*, the desired variations in attaining *thermal* equilibrium were observed superposed on a constant difference between the rates at which *pressure* equilibrium is attained by two wire-gas-wall systems in parallel.

3. *Detail of Method.*—Hydrogen at low pressure is allowed to leak from two Pirani gauge chambers simultaneously, both being connected with a central high vacuum chamber through capillaries of about 60 cm. length and 1 mm.

diameter (fig. 1). At the beginning of each experiment the whole system is filled with pure H_2 to pressures which vary between 0·145 and 0·160 mm. as read by the optical lever micromanometer described in a previous paper.* For accurate filling, without allowing the entering gas to flow over waxed or greased joints or through taps, the usual method of filtering through hot palladium is modified by the device shown in the diagram; in this the temperature of a Pd tube is electrically controlled, the resistance and spacing of the heating coil and the pressure of its hydrogen atmosphere being so designed that a very slight flow can be almost instantaneously started and stopped at will. The platinum filaments of the gauges are placed in adjacent arms of a bridge and balanced, the galvanometer deflection for a given bridge disturbance being reproducible and controllable by means of a potentiometer. The central chamber is then put into communication with a pump which has been maintaining its connections at a steady cathode ray vacuum. The dimensions of

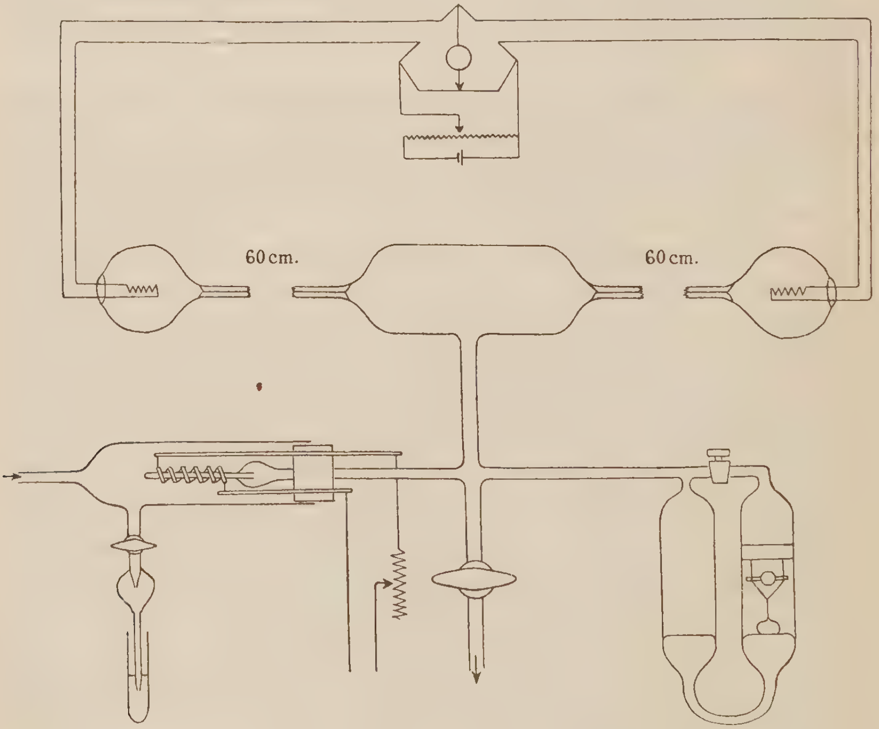

Fig. 1.

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* 'Roy. Soc. Proc.,' A, vol. 123, p. 603 (1929).

the apparatus are such that over $\frac{1}{4}$ hour is needed for the pressure in either gauge to fall from 0·15 mm. to the order of 10^{-4} mm., while the central chamber attains approximate equilibrium with its pump in a fraction of a minute.

During the simultaneous evacuation of the gauge chambers, the bridge balance is temporarily disturbed if the rate of pressure fall is not accurately the same in the two systems. The resulting galvanometer deflection is zero before evacuation begins and reaches zero again when pressure equilibrium is everywhere attained, and hence passes through a maximum, at, say, t (max.) measured from the moment when the central chamber is connected to the high vacuum end of the running pump.

The value of t (max.) will depend on rates of attainment of both pressure and temperature equilibria. These enter, respectively, through two factors :

(A) The purely dimensional difference between the two systems of capillaries and bulbs, leading to a difference between their rates of evacuation.

(B) The time lag in thermal and electrical response to the change of pressure.

Now (B) is a function of α at the wire and the wall, and may vary with different conditions of surface at either of them, but (A) is constant for a given apparatus and can be calculated as follows in order to isolate (B).

Using equations due to Knudsen and to Dunoyer,* we take U the "conductance" of a tube through which a vessel is being evacuated, as the product of mean pressure and the volume of the gas flowing per second under a driving pressure difference of 1 dyne per square centimetre, so that the "output" in time dt is $\mathrm{U}dpdt$. Knudsen verified that

$$\mathrm{U} = \frac{62 \cdot 8 \times 10^3}{\mathrm{M}^{\frac{1}{2}}} \left(\frac{\mathrm{T}}{273}\right)^{\frac{1}{2}} \frac{\mathrm{D}^3}{\mathrm{L}}, \tag{1}$$

where D and L are diameter and length of connecting tube and M the molecular weight of the gas. The condition for the validity of this equation is

$$\mathrm{D}/\lambda < 0 \cdot 4, \tag{2}$$

where λ is the mean free path.

If P be the pressure in the high vacuum chamber, p_t the pressure at time t in a gauge chamber of volume V connected to it through the given tubing, and p_0 the value of p at $t = 0$

$$\frac{p_t - \mathrm{P}}{p_0 - \mathrm{P}} = e^{-\frac{\mathrm{U}}{\mathrm{V}}t}. \tag{3}$$

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* Knudsen, 'Ann. Physik,' vol. 28, p. 75 (1909); Dunoyer, "Vacuum Practice," p. 128 (1926).

In the present case we have two chambers and two capillaries, each system being constructed of roughly the same size but with the following differences, calculated from measurement, using equation (1)

$$V_1 = 101 \cdot 5 \text{ c.c.}, \qquad V_2 = 87 \cdot 5 \text{ c.c.}, \qquad U_1 = 0 \cdot 812, \qquad U_2 = 0 \cdot 801.$$

Hence expression (3) takes the numerical value for the two systems respectively,

$$e^{-0 \cdot 00801\, t}, \qquad e^{-0 \cdot 00917\, t}. \tag{3a}$$

Calculation shows that the difference between these two functions passes through a maximum at

$$t \text{ (max.)} = 120 \pm 3 \text{ seconds.}$$

It must be noticed that the value of t (max.) is not sensitive to errors in U and V. In fact the halving of the dimensional factor in one of the exponents only increases t (max.) to 180 seconds. For this reason we can accept the above dimensions without regarding errors of the absolute length and volume, or even non-uniform deviations of D from 0·10 cm., which measurement showed to cover a range of 1 per cent.

But the disturbance of bridge balance would only be allowed to pass through its maximum at 120 seconds if (B) were negligible.

Experimentally we find t (max.) to vary from about 630 to 330 seconds, reaching finally a limiting value at which it remains approximately constant. In fig. 2 the actual galvanometer deflections of a series are plotted to show the order of accuracy of this " drift " towards smaller values of t (max.). At the beginning of this series the apparatus had not been baked, and no steps had been taken to remove the adsorbed film, mainly of H_2O, which is universally present during the early life of any vacuum tube. Between each of the experiments which show the decrease in t (max.) the apparatus was washed out with pure hydrogen and kept at a cathode ray vacuum. It is known in spectroscopic practice that this cold washing and continued pumping causes a gradual removal of adsorbed layers from the surface, but leaves almost untouched the vapours occluded within the lattice which are only liberated by heat treatment. In fig. 3 t (max.) is plotted against the number of times the system was washed out without intervening contamination. The second series in fig. 3 was obtained after an interval of a fortnight without pumping had enabled a slight liberation of vapour to take place from the interior of the unbaked glass, partially recontaminating the surface.

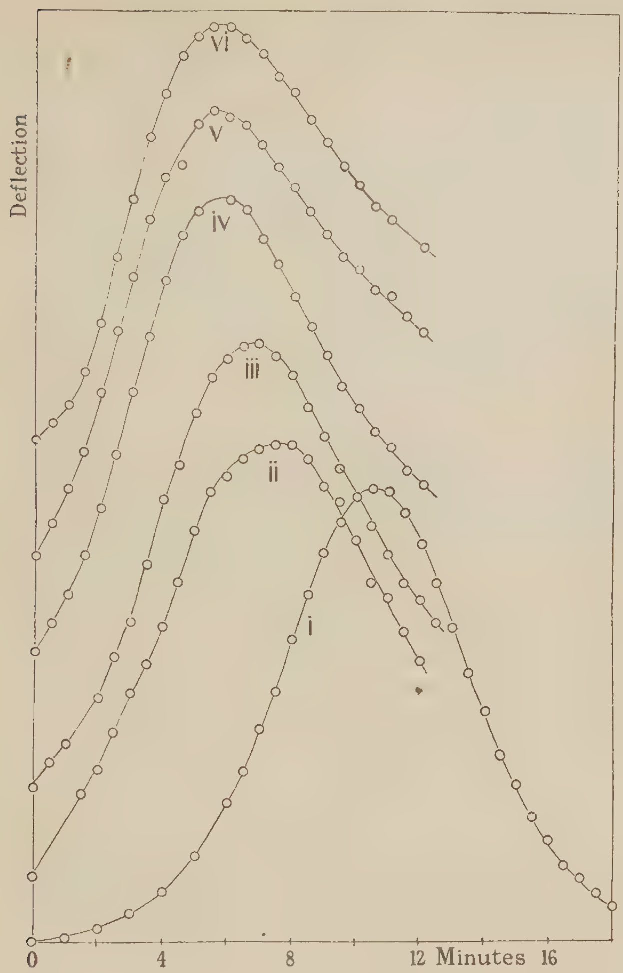

FIG. 2.

Hence we attribute this variable t (max.) to variations in the factor (B). We proceed to find an empirical expression for the variation of t (max.).

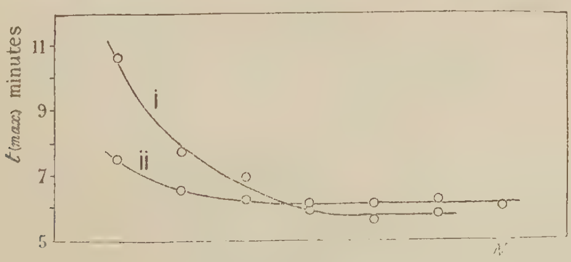

FIG. 3.

4. *Empirical Expression for Variation of t (max.).*—Given two functions, e^{-A_1t} and e^{-A_2t}, the time at which their difference is at a maximum can vary through alteration of the ratio A_1/A_2 or through a variable coefficient common to both exponents. The effect of altering the purely dimensional coefficients in (3*a*), corresponding to A_1 and A_2, has already been seen to be small in considering possible errors in measurement of the apparatus. But a change in "effective" relative dimensions might occur in the following way: there is another type of accommodation coefficient, governing the exchange of *momentum* between gas and solid, which is not necessarily the same as the α discussed in this paper. If this were not the same for each capillary and not constant for either, a variable would be introduced into the relative rates of their evacuation. But such a difference, *e.g.*, in the smoothness of the two capillaries, would have to have the consequence of multiplying the "effective" length of one of them by a factor greater than ten, in order to change the theoretical value of t (max.) into the greatest observed value. Hence we introduce, instead, a variable coefficient of At common to the two functions, remembering that the time lag, in attaining thermal equilibrium, must postpone the response of the galvanometer to any pressure difference which might be due to the purely dimensional ratio A_1/A_2. Hence we represent the results expressed in fig. 2 and fig. 3 by the modification of (3*a*)

$$e^{-0\cdot00801\,t\,(1-\phi)}, \qquad e^{-0\cdot00917\,t\,(1-\phi)}, \tag{3b}$$

where ϕ is some function of the rate at which thermal equilibrium can be established, hence, other things being equal, some function of α at the wire and the wall.

It must be noticed, that, as we are not varying the ratio of the exponents, we are not comparing the value of α for one bulb V_1 with that for V_2, or one capillary with the other, but comparing the mean values of α over both systems for two different occasions.

Hence the use of the capillary leaks and the balancing of two slightly differing gauge systems is to provide a pair of exponential functions; between these there is already a calculable difference due to rates of pressure fall, giving rise to a galvanometer deflection which passes through a maximum. We then observe the modification of that maximum due to variations in the rate of attaining thermal equilibrium. This initial difference of exponentials allows the whole experiment to take the form of measuring a shift in maximum, which is more rapid and accurate than investigating the decay of a single exponential, and is independent of many sources of error arising in the study of accommodation coefficients; for instance, a sensitive electrical system can be employed and the filament temperature kept low enough to neglect volatilisation. The method should therefore detect surface changes which might otherwise escape notice.

To determine the order of magnitude of ϕ, and to ensure that it is single-valued for any given variation of t (max.), the two filaments were finally connected in series and the same process of evacuation again measured. Let d_0 be the galvanometer deflection finally approached in the attainment of thermal and pressure equilibrium; this can be obtained logarithmically and need not be of great accuracy. Then for an experimental expression comparable with (3), we take

$$(d_0 - d_t)/d_0.$$

This is plotted in fig. 4 and compared with theoretical and empirical curves. If thermal equilibrium were instantaneously established, the curve would have followed the mean of the exponentials (3a)

$$e^{-0\cdot00859\,t}.$$

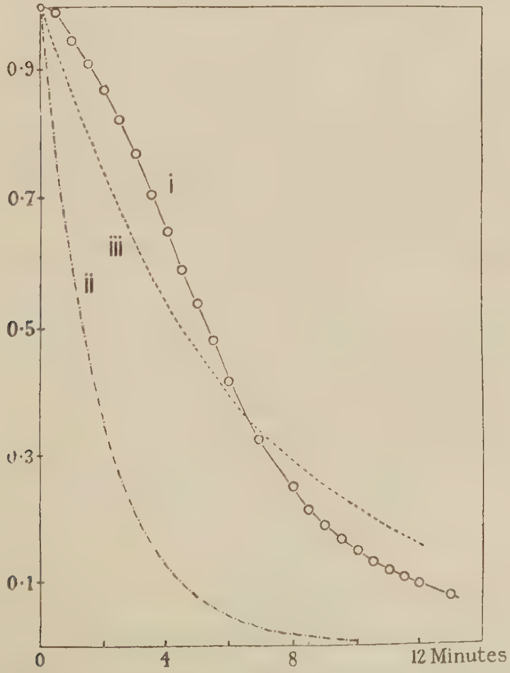

FIG. 4.—(i) $(d_0 - d_t)/d_0$, (ii) $e^{-0\cdot00859\,t}$, (iii) $e^{-0\cdot00859\,t\,(1-0\cdot7)}$

The lack of agreement shown in the graphs is obviously to be expected from considerations of two kinds :—

(i) A finite time is needed to reach thermal equilibrium, *i.e.*, $0 \cdot 00859t(1 - \phi)$ must be substituted for $0 \cdot 00859t$.

(ii) The experimental curve is not itself a pure exponential. Under this heading come the facts that the low pressure is not immediately established in the central chamber, that condition (2) is not at once fulfilled, that towards the end of the process P is no longer negligible compared with p, and that galvanometer deflections are not calibrated directly in terms of pressure.

We do not pursue (ii), since they do not affect t (max.). We find, however, that the nearest *pure* exponential to the experimental curve is

$$e^{-0 \cdot 00859\, t(1-0 \cdot 7)},$$

which establishes the order of magnitude of ϕ. Assuming this order of magnitude, we determine the variation of ϕ, computing differences between the two functions (3*b*), and verifying that the following are the values of t (max.) corresponding to certain simple values of ϕ :—

ϕ	=	0	2/3	3/4	4/5
t (max.)	=	2	6	8	10 minutes.

To the approximation represented by the simple values of ϕ, these cover the experimental range of fig. 2, in which t (max.) fell from $10\frac{1}{2}$ minutes to below 6 minutes and remained nearly constant at that value. The graphs indicate that there is no need at present for more precise specification of the value of ϕ.

5. *Filament Variations.*—Under the conditions of these experiments the transfer of heat, H units per second per unit area, from filament to wall, can be described by Knudsen's equation. This may be written as follows in a form independent of such conditions as are here constant.

$$H = \frac{\alpha}{2 - \alpha}\, p \frac{T_1 - T_2}{T^{\frac{1}{2}}} SC, \qquad (4)$$

T_1, T_2, and T are filament, wall, and mean temperatures respectively, S is a constant depending on molecular weight and specific heats of the gas, and C depends only on the dimensions of the apparatus. Knudsen's equation only refers strictly to a system in which α is the same for both the hot and the cold solid. Since α varies with temperature, this condition is not quite fulfilled even when the two solids are made of the same material. But the equation has been of sufficient accuracy for the degree of approximation to which accommodation coefficients have hitherto been studied; it may be used in the manner specified below if α only varies over a small range and is not greatly different for the two solids, and if the area of the hot wire is small compared with that of the cold glass. In considering the extension of this method to other substances, it may be proved that, if the above conditions were relaxed, $\alpha/(2-\alpha)$ would have to be replaced by the following expression:

$$\frac{(\alpha_1 T_1 - \alpha_2 T_2)/(T_1 - T_2)}{2 - (\alpha_2 T_1' - \alpha_1 T_2')/(T_1' - T_2')},$$

in which α_1, α_2 are the accommodation coefficients for the two bodies at temperatures T_1 and T_2 respectively, the temperatures of molecules leaving the two bodies are T_1' and T_2', and the temperature of molecules on approaching the one body is equal to that on leaving the other.

A control experiment was carried out to determine the maximum effect of any change in filament temperature due to changes in the external circuit. The potentiometer supplying the bridge was adjusted over a range more than sufficient to cover all potential fluctuations during the sequence of experiments described. This was found to effect a total variation of 4 per cent. in t (max.), whereas the sequence in fig. 2 involves a variation of the order of 70 per cent.

Apart from such changes in temperature due to the external circuit, both the temperature and resistance and the accommodation coefficient at the filament might alter if any secular change occurred in the physical and chemical properties of the platinum.

The maximum extent to which such changes can occur in the present experiments and affect the thermal exchange between filament and gas, is limited by the following precautions taken:—

(i) The risk of gas impurity from *outside* was eliminated by the method of hydrogen introduction described, and by the fact that the glass sealing, etc., had been perfected until the whole system showed no sign of external leak over a period of several weeks.

(ii) Before the experiments were begun, the filaments in series were glowed in hydrogen. This enabled them to emit their initially occluded gases, and to absorb as much hydrogen as they could at a temperature higher than that at which they were to be worked. After t (max.) had reached approximate stability, they were again glowed, and the experiments then repeated, without any difference in its value being observable.

(iii) The total resistance of the filaments in series, at a given gas pressure, had a range of $2\frac{1}{2}$ per cent. throughout their life in hydrogen, including outgassing. The ratio of their resistances was between $1/0 \cdot 980$ and $1/0 \cdot 995$ throughout.

(iv) It is obvious that even after the gradual freeing of the walls from vapour, more could be liberated by heating, since the glass had not previously been baked. To determine whether any change in the *filaments* could be attributed to the liberation of vapour from the walls, *e.g.*, oxidation through H_2O, the glass was finally heated sufficiently to allow fresh diffusion of this from its interior. The resistance and the value of t (max.) were then redetermined, without any change being discovered. Hence it is not possible to attribute the progressive variation of t (max.) to any effect on the wire itself of the liberation which had been proceeding during cold washing with hydrogen.

(v) Effects of dissociation and adsorption can be eliminated, since the only electric discharge (used to verify spectroscopic purity) was at the pump end of the flowing gas stream.

From these precautions we conclude that the progressive decrease in t (max.) is mainly due, not to changes in temperature or accommodation coefficient at the filament, under constant conditions of external circuit and gas pressure, but to such agency in the attainment of thermal equilibrium as depends on the efficiency of collision with the glass walls. The decrease progresses to a limit with the cold washing with hydrogen; accordingly we consider the sequence of values of t (max.), expressible in terms of ϕ, as representing the change of accommodation coefficient at the glass surface, known to be initially covered with an adsorbed film and emerging gradually from its more detachable impurities.

Hence, in equation (4), α at the filament, as well as the pressure and temperature variables, are now to be included under the constants, and we write

$$\phi = f(\alpha)_{\text{glass}}.$$

The absolute value of α cannot be determined in the present experiments, but the form of the control which it exerts over ϕ can be obtained in the following manner.

6. *Relation of t (max.) and ϕ to α at the Glass Surface.*—Let the true fall of pressure in either gauge be expressed by an equation of the form

$$p = p_0 e^{-xt}.$$

The pure exponential which will approximate most nearly to any complex law of apparent pressure fall may be written

$$p' = p_0 e^{-x(t-\psi)},$$

since at any instant t, in the progress towards a pressure equilibrium, we observe the stage which actually had been reached at some time t', when

$$\psi = t - t',$$

ψ is a time lag, proportional to the time taken to reach some definite stage in the progress towards a thermal equilibrium; this time, t_θ, is inversely proportional to the mean rate of heat transfer H, so that

$$\psi \propto t_\theta \propto 1/\mathrm{H}.$$

Any rate of heat transfer by conduction at low pressures depends on the appropriate value of the pressure; hence, if the latter is varying, ψ is not a constant but depends on the stage already reached in the equalisation of pressures throughout the apparatus. The lag becomes greater as the pressure is decreased, and in a simple treatment of the subject it will probably be sufficient to take ψ as proportional to t. If we write

$$\psi = \kappa t,$$

κ may then be identified with the empirical quantity ϕ already determined from the experiments. Hence, if we choose two of the experiments on t (max.), performed under two sets of conditions A and B respectively,

$$\frac{\phi_{\mathrm{A}}}{\phi_{\mathrm{B}}} = \frac{\mathrm{H}_{\mathrm{B}}}{\mathrm{H}_{\mathrm{A}}}.$$

From equation (4), having regard to the quantities shown in the preceding section to be approximately constant, we have, therefore,

$$\frac{\phi_{\mathrm{A}}}{\phi_{\mathrm{B}}} = \frac{\alpha_{\mathrm{B}}(2 - \alpha_{\mathrm{A}})}{\alpha_{\mathrm{A}}(2 - \alpha_{\mathrm{B}})},$$

relating the ratio of empirical constants to accommodation coefficients at the glass surface in its different stages of freedom from initially adsorbed layers.

For instance, in the present experiments, the progressive change of t (max.)

from 10 minutes to 6 minutes roughly, expressible as a 20 per cent. decrease in ϕ, corresponds to an increase of approximately 17 per cent. in α for H_2 at the glass surface as the latter is purified.

Knudsen determined α for H_2 on glass, obtaining 0·26. If this be taken to represent the initial value at glass for which outgassing has not been carried out, the removal of such adsorbed vapour as can be liberated by prolonged washing *in vacuo* is shown in the present experiments to result in an increase of α to between 0·30 and 0·31.

I am very grateful to Prof. S. W. J. Smith, F.R.S., for his generosity in enabling me to carry out these experiments, and to Mr. G. O. Harrison for the constant use of his skill and experience in vacuum technique.

Experiments on the Exchange of Energy between Gas, Solid and Adsorbed Layer in vacuo—II. *The Effect of a Deposited Monomolecular Layer on the Efficiency of Molecular Collisions.*

By M. C. Johnson, M.A., M.Sc., Lecturer in Physics, University of Birmingham.

(Communicated by S. W. J. Smith, F.R.S.—Received March 29, 1930.)

1. *Introduction.*—A previous paper* has described a method of detecting small changes in the thermal efficiency of encounters between gas molecules and a solid surface. This efficiency determines the rate at which conductive equilibrium is re-established between filament and walls of a Pirani gauge chamber, when the pressure is altered within a range of 10^{-1} to 10^{-4} mm., the medium of thermal exchange being hydrogen. In the paper it was shown that when two such gauges are balanced in a resistance bridge and simultaneously evacuated through long capillaries, the disturbance of balance, due to unequal rates of gas flow and to the finite time for reaching thermal equilibrium, passes through a maximum at a characteristic time t (max.). t (max.) has a lower limiting value of 120 seconds, dependent on the dimensions of the apparatus, and above that its value varies with the thermal efficiency of the gas-solid collisions; it was shown that a decrease in t (max.) from 10 minutes to 6 minutes, consequent on outgassing, corresponded to a 17 per cent. increase

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* Part I, *supra*, p. 432.

in the accommodation coefficient "α," as the adsorbed layers were removed from the glass.

In the present paper the method is extended to determine the change in accommodation coefficient for H_2 when a hydrogen layer of monomolecular thickness has been deposited on the glass. Since no chemical reaction can be invoked under the conditions below specified, these experiments isolate the purely physical part of the changes in α which accompany the formation of such active monomolecular layers as are discussed in the chemistry of heterogeneous reactions.

2. *Deposition and Measurement of the Hydrogen Layer.*—It was shown in another previous paper* that the adsorption of hydrogen on a baked glass surface *in vacuo*, first studied by Langmuir with tungsten filaments, can be made to take place in such a way as to have a definite saturation density, and to be independent of the presence of metals. Fig. 1 shows the experimental arrangement for applying such a method to the apparatus we had used for comparing

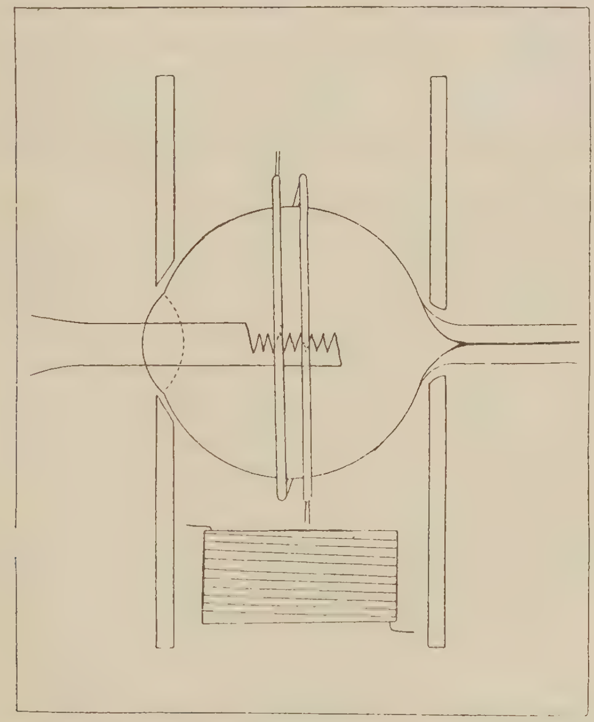

FIG. 1.

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* 'Roy. Soc. Proc.,' A, vol. 123, p. 603 (1929).

accommodation coefficients; the bulb and its surroundings must be supposed duplicated and connected to each end of the capillary system illustrated in Part I. The process of depositing hydrogen from the gaseous phase upon the walls of these bulbs was carried out as follows :—

(i) The Pirani gauge chambers were baked at about 200° C. during an hour's evacuation, the pressure being below that permitting any discharge in the indicator tube attached to the apparatus.

(ii) The system was isolated from the pumps and, when cool, was filled to 0·147 mm. with pure dry H_2 by means of the electrically controlled palladium furnace described in Part I.

(iii) A high-frequency electrodeless discharge was induced in the two Pirani chambers together, by passing through their surrounding coils the output from an oil condenser charged from a spark gap. The pressure fall, measuring the resulting deposition of dissociation products on the walls, was traced by the method described in the paper on adsorption. Saturation was found to be complete in 6 minutes, though sufficient gas was then left for the discharge to be apparently undiminished in intensity.

Fig. 2 shows the completion of this saturation, and may be compared with the curves given in the other paper: the less rapid pressure fall in this case

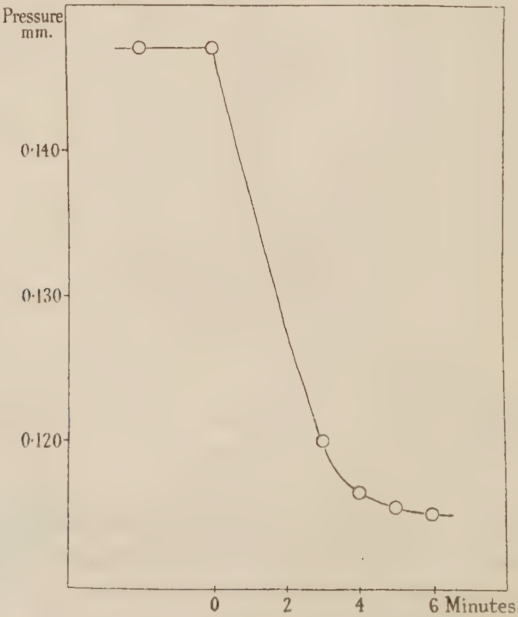

Fig. 2.—Loss of H_2 in electrodeless discharge.

is due to the presence of the capillary inflow from the central reservoir, whereas previously a closed system had been employed. For this reason no attempt was made to determine the initial rate of fall, which would not be open to the same interpretation as those previously illustrated. When the pressure had ceased to fall, the discharge was stopped and H_2 admitted, until equilibrium was everywhere reached at the same initial value of 0·15 mm. from which evacuation had commenced in all the experiments of Part I.

The surface density of the hydrogen thus deposited is calculated, and the layer shown to be monomolecular in thickness, as follows. We assume, with Langmuir, that it is the atom only which condenses, and so take the number of particles adsorbed as twice the number of molecules lost to the pressure.

Initial pressure, in mm.	0·147	0·087	0·090
Final pressure, in mm.	0·115	0·0485	0·075
Volume of region of loss of pressure, in cm.^{3}	487	198	164
Area for adsorption, in cm.^{2}	194	85	52
Mean surface density of layer, per cm.^{2}	$5 \cdot 3 \times 10^{15}$	$5 \cdot 9 \times 10^{15}$	$3 \cdot 2 \times 10^{15}$

In the last two columns are the results obtained with apparatus of quite different volume and shape, from the previous paper, indicating that the saturation density is of the same order under the very dissimilar conditions. If the monomolecular layer were packed until Bohr orbits were in contact, the maximum surface density would be $8 \cdot 9 \times 10^{15}$.

When the two filaments were balanced in a resistance bridge, the Pirani gauge chambers could be considered as in the state corresponding to the commencement of any of the determinations of *t* (max.) in Part I, with the difference that in the present case the surface of the glass had been freed from adsorbed layers, mainly of H_2O, and on it deposited the monomolecular layer of hydrogen atoms. We proceed to determine the effect of this layer on the accommodation coefficient, or the thermal efficiency of collisions made with the covered surface by impinging H_2 molecules.

3. *Measurement of t (max.).*—Simultaneous evacuation of the two Pirani chambers and capillaries is now carried out, with the precautions detailed in Part I, and the galvanometer deflections recorded; these denote the temporary disturbance of bridge balance between the resistances of the two filaments, and depend, in the manner discussed in Part I, on the rates of attainment of pressure and thermal equilibrium. The resulting curves relating deflection to time are not reproduced here, since they are of the type already illustrated

in Part I. Fig. 3 shows the variation in t (max.) obtained from the deflections, consequent on the different treatments to which the glass surface has been subjected ; each point represents one of the successive states of the gas-solid interface, determined by the course of measurements made during each evacuation from 0·15 mm.

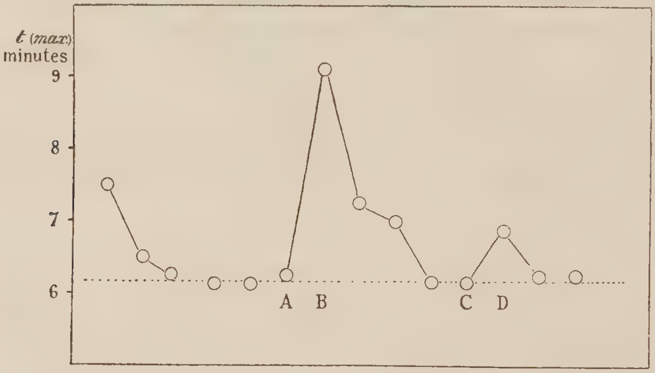

Fig. 3.—Variation of t (max.) with surface condition. Atmospheric exposure between A and B ; hydrogen deposit between C and D.

The stable value of t (max.) corresponding to a "clean," or thoroughly baked and outgassed, surface is just above 6 minutes, with a variation of 6·1 to 6·25, which is of the order of the errors discussed in Part I. The deposit of new surface layers consequent on a re-exposure to the atmosphere raises the value to over 9 minutes. The initial value for new and uncleaned glass obtained in Part I was nearly 11 minutes. The return to 6 minutes is always reproducible by thorough washing or baking in pure dry H_2. The occasion when the monomolecular layer of H_1 had been deposited provided a value of t (max.) intermediate between those for the contaminated and the clean states, t (max.) occurring in this instance alone at nearly 7 minutes, and returning after washing to the previous constancy not far from 6 minutes.

It may be noticed that the lowest value of t (max.) ever reached, just below 6 minutes, is never quite regained after the early history of the apparatus in Part I ; continued treatment over a period of months must, of course, decrease the gas content of the interior of the solid, and hence the concentration of diffusable products below the actual surface and the consequent packing of the outermost solid layer ; from this some secular variation is to be expected which is not interpretable. The secular variations in the adsorption of H_1 were discussed in the paper on that subject, and preclude giving any interpretation to repeated deposits of atoms, which is therefore not attempted.

4. *The Variation of the Accommodation Coefficient.*—In Part I the experimental variation of t (max.) was related through an empirical function ϕ to a variation in the accommodation coefficient α for H_2 at the glass surface. Since the changes there recorded between the initial and finally outgassed states of the glass represented a 17 per cent. increase in α, the smaller change due to the deposition of the monomolecular layer of H_1 represents a decrease of 3 per cent. or 4 per cent. from the value for a "clean" surface. Hence if Knudsen's value

$$\alpha = 0 \cdot 26$$

be accepted as representing the state of ordinary untreated glass, and it rises to

$$\alpha = 0 \cdot 305 \pm 0 \cdot 005$$

when the initial layers, mainly H_2O, are removed, the present experiments indicate that it decreases slightly, say, to

$$\alpha = 0 \cdot 295 \pm 0 \cdot 005$$

when the surface is covered by a layer of H_1 atoms.

This decrease is well outside the limit of experimental error, since it involves a change of 3/4 minute in the value of t (max.). In considering the possible errors in isolating this change at the glass from changes in the filaments, etc., the reproducible return to a stable value of t (max.) shown in fig. 3 must be considered in relation to the precautions discussed in Part I. This precludes there being any effect of the dissociated gas on the platinum, which had not therein been taken into account.

5. *Application to Physical Theory of the Accommodation Coefficient.*—It is clear that any accommodation coefficient may cover a variety of physical and chemical mechanisms, and will be very dependent on any reaction or attractive bond between the impinging molecules and the field of the atoms in the surface layer. But in the present case the adsorption of H_2 is very slight, whether on the clean glass, the layer of H_1, or the water-vapour film initially present on most glasses; since no reaction takes place, it is worth enquiring whether we have here a case in which the accommodation coefficient describes, in the main, a purely physical mechanism of elastic collision. This may be tested in terms of the theory of elastic exchange of energy between gas and solid first put forward by Baule and developed by Langmuir.* If m_1 be the mass of an

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* Baule, 'Ann. Physik,' vol. 44, p. 145 (1914); Langmuir, 'Phys. Rev.,' vol. 8, p. 149 (1916).

impinging gas molecule, and m_2 the mass of a vibrating particle in the surface layer, the energy exchange between them depends on the value of these masses through the relation

$$\alpha = 1 - \beta n$$

in which $\beta = (m_1^2 + m_2^2)/(m_1 + m_2)^2$ and $1 - n$ is the fraction of the impinging molecules which is capable of remaining on the surface for a time long compared with the duration of a single collision.

Langmuir pointed out the impracticability of applying this simple theory in most cases likely to be of interest to the student of heterogeneous equilibria; the variation of n is itself one of the unknown quantities generally sought, and forces of valency may entirely obliterate the elastic character of the impact. But in the present problem of comparing accommodation coefficients of an almost non-adsorbing and non-reacting gas, the discarded theory is not necessarily too simple. We have only to enquire whether, by assuming any value of n which is a large fraction and which is constant for all the varieties of surface discussed, we can calculate a range of α in agreement with the present experiments. Now the mainly amorphous structure of a soda-lime glass must present a surface in which the average mass of separately vibrating centres will not be far from the weighted mean of all its atomic constituents; we take, therefore, $m_2 = 20$, and note that considerable latitude in composition around 70 per cent. SiO_2, 15 per cent. Na_2O, 10 per cent. CaO, will introduce into it only small variations. For hydrogen $m_1 = 2$, and we choose $n = 0{\cdot}84$; we calculate the accommodation coefficients by means of the above simple elastic equations, assuming that the H_1 atom and the H_2O molecule each merely load the vibrators in the solid lattice, and that the H_2 molecules rebound from each lattice point. For comparison, in the last column, are the values determined in the present experiments, using, as before, Knudsen's determination as the initial value for glass that has not been baked and outgassed.

	From elastic theory.	From experiments.
α for H_2 at "clean" glass	0·30	0·305 ± 0·005
α for H_2 at H_1 covered glass	0·29	0·295 ± 0·005
α for H_2 at H_2O covered glass	0·24	0·26

The variation of accommodation coefficient deduced from variations in t (max.) in these experiments is therefore in agreement, to the order of its own accuracy, with the hypothesis that in these cases elastic collision is the principal mechanism of energy exchange, and that not only the H_1 but also the H_2O

form monomolecular attachments to the solid lattice. It may be noted that recent evidence* supports this latter, water vapour only forming multimolecular layers on glasses that have been acid treated. The discrepancy between Langmuir's monomolecular theory and the large amounts of H_2O often obtained as desorption products is probably to be resolved in this way, by the history of the glass, and by diffusion from its interior.

The Thermal Decomposition of Ethyl Ether on the Surface of Platinum.

By E. W. R. Steacie and H. N. Campbell, Physical Chemistry Laboratory, McGill University, Montreal.

(Communicated by A. S. Eve, F.R.S.—Received April 7, 1930.)

Introduction.

It is of considerable interest to compare the velocities of homogeneous and heterogeneous gas reactions. In general homogeneous bimolecular reactions tend to become unimolecular in the presence of a catalyst, and the heat of activation falls to about one-half. This has been shown to be the case in the decomposition of nitrous oxide, hydrogen iodide, and ammonia.†

The question arises as to what is the effect of a catalyst on a homogeneous unimolecular reaction. The decomposition of gaseous diethyl ether was chosen for investigation on account of its simplicity; and an attempt has been made to compare the heterogeneous decomposition on the surface of platinum with that of the homogeneous reaction which has been investigated by Hinshelwood.‡

Apparatus.

The ether was decomposed on an electrically-heated platinum wire stretched axially in a bulb of about 100 c.c. capacity. The progress of the reaction was followed by observing the rate of increase in pressure by means of a capillary manometer. A nichrome heating element was wound on the manometer, which was kept at a temperature of about 45° C. to prevent condensation of the ether. The reaction bulb was immersed in a thermostat at 40° C.

The temperature of the filament was obtained by measurement of its

* 'J. Am. Chem. Soc.,' vol. 50, p. 2987 (1928).

† Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press (1926).

‡ 'Roy. Soc. Proc.,' A, vol. 114, p. 84 (1927).

resistance. The temperature coefficient of resistance was measured by a separate experiment at 0° C., 100° C., and 444° C. using about 3 feet of the wire and a Wheatstone bridge. A piece of this wire was used to make the filament. After it had been sealed into the bulb the resistance was measured by the ammeter-voltmeter method.* The temperatures calculated from the resistance were checked by means of an optical pyrometer. During the course of an experiment the temperature of the filament was kept constant by hand regulation of the current by means of a rheostat.

The ether used was made by the Mallinckrodt Chemical Company, and was redistilled from metallic sodium.

The Course of the Reaction.

Hinshelwood (*loc. cit.*) found that ether decomposes homogeneously in accordance with the equation

$$C_2H_5 . O . C_2H_5 = 2CH_4 + CO + \tfrac{1}{2}C_2H_4.$$

This should give a product consisting of CO, 28·6 per cent., CH_4, 57·1 per cent., C_2H_4, 14.3 per cent. Some sample analyses of the products of the heterogeneous reaction are given below :—

Reaction bulb No. 1. Temperature 800° C. Initial pressure 75 mm.

	per cent.
CO	24·0
C_2H_4	24·0
CH_4	52·0
CO_2	0·0

Reaction bulb No. 2. Temperature 750° C. Initial pressure 200 mm.

	per cent.
CO	24·2
C_2H_4	21·4
CH_4	54·2
CO_2	0·4

Reaction bulb No. 2. Temperature 650° C. Initial pressure 150 mm.

	per cent.
CO	25·6
C_2H_4	15·0
CH_4	59·1
CO_2	0·0

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* See Hinshelwood, 'J. Chem. Soc.,' vol. 127, p. 327 (1925).

If the decomposition follows the same course as the homogeneous reaction, the increase in pressure at the end of the reaction should be 250 per cent. Some of the observed values for the final increase in pressure are given below.

Temperature.	Initial pressure.	Final pressure.	Per cent. increase.
° C.	mm.	mm.	
600	75	260	247
800	150	522	248
800	75	268	256
800	50	177	264

The course of the reaction thus seems to be the same as that of the homogeneous reaction. The higher proportion of ethylene is probably caused by a side reaction forming ethylene and water:

$$C_2H_5 . O . C_2H_5 = 2C_2H_4 + H_2O.$$

The amount of this reaction, however, is small, and since it leads to almost the same pressure increase as the main reaction it has been neglected in the calculations.

The Order of the Reaction.

Some sample pressure-time curves are shown in fig. 1. In Table I the data are given for a typical run.

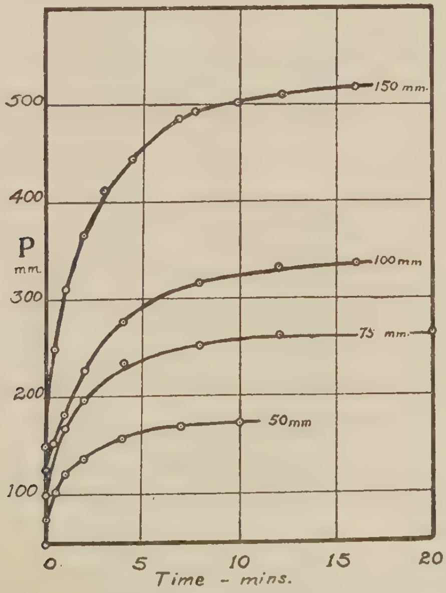

FIG. 1.—The Rate of Decomposition at 800° C. Reaction bulb No. 1.

Table I.—Reaction Bulb No. 1. 700° C.

Time.	Pressure.	Per cent. decomposed.	K.
minutes.	mm.		
0	50	0·0	—
5	62	9·6	0·0201
10	70	16·0	0·0174
15	79	23·2	0·0176
20	87	29·6	0·0176
25	92	33·6	0·0164
30	98	38·4	0·0162
40	105	44·0	0·0166
50	117	53·6	0·0153
60	125	60·0	0·0152
70	131	64·8	0·0148
80	136	68·8	0·0144

The constant K, shown in the last column, is that calculated for a unimolecular reaction. It will be seen that there is a considerable drift in the value of K, particularly towards the end of the reaction. This will be discussed later.

A much more satisfactory criterion of the order of a reaction is the time required for a given fraction of the reactant to decompose. The times required for a 50 per cent. increase in pressure (*i.e.*, for 26·6 per cent. of the reactant to decompose) are shown in Table II.

Table II.—Time for 50 per cent. increase in pressure.

Bulb No. 1. 750° C.								
Initial pressure (mm.)	23·8	60	114	321	553			
Time (minutes)	6·3	3·3	3·2	3·1	3·4			
Bulb No. 1. 700° C.								
Initial pressure (mm.)	23	50	100	150	200	330	360	566
Time (minutes)	20·0	16·8	14·1	12·4	11·5	9·7	9·7	9·7
Bulb No. 2. 650° C.								
Initial pressure (mm.)	200	300	400					
Time (minutes)	34·0	25·0	21·0					
Bulb No. 2. 675° C.								
Initial pressure (mm.)	32	37	84	149	172			
Time (minutes)	10·2	9·6	8·4	7·0	7·3			
Bulb No. 2. 700° C.								
Initial pressure (mm.)	54	64	175	303	400			
Time (minutes)	2·4	2·5	2·9	2·5	2·6			

The data given in Table II are plotted in fig. 2. It will be noticed that the time for 50 per cent. increase in pressure is independent of the concentration (at high pressures) and hence the reaction is unimolecular. At low pressures, however, the velocity constant falls off and the reaction tends to become bimolecular. This is in agreement with the data in Table I, since the velocity constant tends to fall towards the end of the reaction when the partial pressure of the reactant is low. Hinshelwood has observed the same behaviour with the homogeneous reaction. It is to be noted that the pressure at which the falling off begins increases with decreasing temperature.

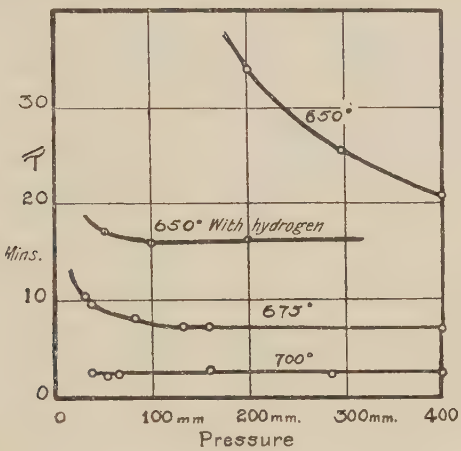

FIG. 2.—Time for 50 per cent. increase in pressure.

The Effect of Added Gases.

Several experiments were made in the presence of excess of the decomposition products. They were found to have no effect on the rate, as is the case with the homogeneous reaction.

The effect of hydrogen, on the other hand, is marked. In the presence of a sufficient amount of hydrogen the rate of reaction does not fall off at low pressures. The effect of added hydrogen is shown in Table III, and for comparison the results are plotted in fig. 2. In the homogeneous reaction the addition of hydrogen has an identical effect.

Table III.—The Effect of Added Hydrogen.

Initial pressure of reactant.	Hydrogen pressure.	Time for 50 per cent. increase in pressure.	
		With H_2.	Without H_2.
mm.	mm.	minutes.	minutes.
50	165	17·2	over 100
100	215	16·1	ca. 50
200	265	16·3	34
300	340	20·5	28

The Temperature Coefficient.

The times for a 50 per cent. increase in pressure at various temperatures are given in Table IV.

Table IV.—Time for 50 per cent. increase in pressure. Initial pressure = 400 mm.

——	Temperature.	Time.
	° C.	seconds
Bulb No. 1	800	58
	750	192
	700	585
Bulb No. 2	825	6·5
	800	11·0
	775	17·8
	750	28·6
	725	76
	700	164
	675	415
	650	1260
	625	3000

In fig. 3 the logarithm of the time for a 50 per cent. increase in pressure is plotted against the reciprocal of the absolute temperature. The values for each bulb fall well on straight lines in the region from 700 to 825° C., but there is some deviation from linearity at lower temperatures. The heat of activation calculated from the slope of the lines is 52,000 calories per gram molecule for both bulbs.

The apparent deviations from the Arrhenius equation are due to the fact that the pressure at which the velocity constant falls off increases with decreasing temperature. The values given in fig. 3 are for an initial pressure of 400 mm. At low temperatures the falling off pressure becomes higher than this and hence the reaction is no longer unimolecular. At 650° C. the deviation from linearity is quite large, but if the value of the time obtained in the presence of hydrogen is used the deviation disappears.

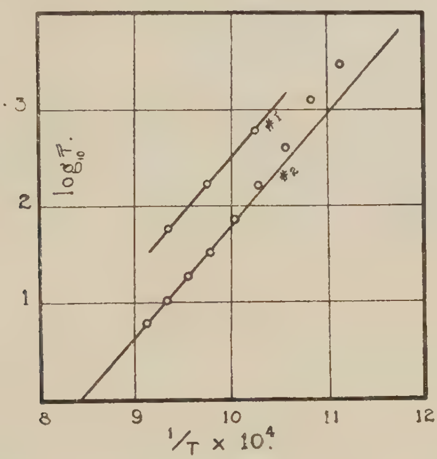

FIG. 3.—The Temperature Coefficient of the Reaction Velocity. Initial pressure = 400 mm.

Comparison with the Homogeneous Reaction.

In comparing the decomposition on the surface of platinum with the homogeneous reaction, the following points are to be noted :—

(*a*) The analyses of the products of the reaction indicate that the surface reaction follows the same course as the homogeneous reaction.

(*b*) The heat of activation of the surface reaction is 52,000 calories ; that of the homogeneous reaction is 53,000. These are identical within the experimental error.

(*c*) The velocity constant falls off at low pressures as in the homogeneous reaction.

(*d*) The addition of hydrogen prevents the falling off of the velocity constant at low pressures in both the surface and the homogeneous reactions.

(*e*) The addition of the products of the reaction has no effect in either case.

The combination of all these facts seems to indicate that the platinum has no catalytic effect on the reaction ; in other words it is not necessary for a molecule to be adsorbed in order that it shall react. This leaves only two possibilities : either the molecule receives its energy directly from the filament and reacts in the same manner as if it had got it from other molecules, or else it receives its energy from other molecules which, in turn, obtained it from the filament. These two possibilities are actually the same, involving only the question as to whether the molecule gets its energy directly or indirectly. Hence the reaction is to be regarded as taking place homogeneously in a thin layer of hot gas surrounding the filament.

After this investigation had been commenced a paper appeared by Taylor* on the decomposition of acetone on the surface of platinum. He also comes to the conclusion that the reaction takes place homogeneously in the gas surrounding the filament. It seems therefore to be difficult, or impossible, to catalyse a homogeneous unimolecular reaction.

Summary.

An attempt has been made to investigate the heterogeneous thermal decomposition of diethyl ether on the surface of platinum. It has been found that the platinum does not catalyse the reaction which therefore takes place homogeneously in the hot gas surrounding the filament. All the observed results are the same as those for the homogeneous decomposition, except that the pressure at which the velocity constant falls off increases considerably with decrease in temperature.

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* ‘J. Phys. Chem.,’ vol. 33, p. 1793 (1929).

Passage of Slow β-Particles through Matter—Production of Branches.

By E. J. Williams, Manchester University.

(Communicated by W. L. Bragg, F.R.S.—Received May 6, 1930.)

Important information about the loss of energy by β-particles may be obtained by studying the secondary electrons with large energy which are occasionally produced and which appear in a Wilson cloud photograph as branches to the main β-particle tracks. In the present work the number of branches produced by β-particles with energy of about 20,000 volts in nitrogen and oxygen has been observed and also the energy relations which exist in branch collisions. For small angles of scattering of β-particles by electrons the formulæ derived on the new quantum theory and on the classical theory agree, but for large angles of scattering such as those concerned in the branch collisions investigated here there is an appreciable difference. This difference arises from the application in the case of the quantum theory calculations of Pauli's exclusion principle to free electrons (*i.e.*, aperiodic systems). The results of the present experiments support the quantum theory formula.*

Previous observations on the production of branches by slow β-particles have been made by C. T. R. Wilson.† His observations on the frequency of branches do not apply to sufficiently large angles of scattering to test the difference between the classical and quantum theory formulæ and the results obtained are not very conclusive.

The present results for the energy relations in branch collisions show that within experimental error a β-particle loses an amount of energy in a branch collision equal to that acquired by the branch electron. According to certain observations by Wilson the momenta of the β-particle and branch electron do not obey a similar relationship. The significance of these results, and the classification of collisions proposed by the writer in a previous paper on the straggling of β-particles are mentioned at the end of this paper.

The results for the frequency of branches are of use in finding how the total loss of energy by slow β-particles—represented by the "stopping power"—is distributed between the different kinds of collisions. This distribution is of considerable theoretical importance and data in connection with it for fast β-particles were recently obtained by the writer in a study of the straggling of β-particles* and in cloud experiments on primary ionisation and branches carried out with F. R. Terroux.† The collective significance of these separate investigations on slow and fast β-particles will be considered in a later paper. The present discussion is confined to the points mentioned above.

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* These observations were carried out in Manchester in 1927, before the new quantum theory calculations were made, and the results were first mentioned in a Ph.D. thesis (Cambridge) presented in September, 1929.

† 'Roy. Soc. Proc.,' A, vol. 104, pp. 1, 192 (1923).

§ 2*a*. *Frequency of Branches. Theoretical Requirements.*

For a β-particle traversing an atmosphere of free electrons initially at rest the average number of collisions per unit length of path in which the particle loses energy between Q and Q + dQ is on the classical theory given by

$$\phi(Q)\,dQ = (2\pi e^4 n/mv^2)\,dQ/Q^2, \qquad (1)$$

where n is the number of electrons per unit volume, v is the velocity of the β-particle and e and m are the electronic charge and mass respectively. If the electrons traversed are initially in motion, possessing an average kinetic energy equal to ε, then the value of $\phi(Q)$ is increased by the factor $(1 + 4\varepsilon/3Q)$.‡ The present observations were made on the branches produced by β-particles traversing light elements such as oxygen and nitrogen. The kinetic energy of the extra-nuclear electrons in these elements is very small compared with the energy of the branches, and the above correcting factor for the motion of the atomic electrons may be neglected. It may also be shown that in branch collisions the effect of atomic binding forces is negligible. For if we denote by q the classical distance of nearest approach of the β-particle and the "knocked" electron then

$$q^2 = 2e^4/mv^2Q \quad \text{approximately}. \qquad (2)$$

For β-particles with 20,000 volts energy, and branches with 5000 volts energy, such as are dealt with in the present experiments, the distance of approach given by (2) is $1 \cdot 4 \times 10^{-11}$ cm. This is about 50 times less than the inter-electronic and electron-nucleus distances for the innermost electrons of oxygen and nitrogen. The "time of collision" is approximately represented by q/v and this is less than 1/1000th of the natural period of the same electrons. In order that atomic binding forces should play an appreciable part in a collision the "time of collision" must be comparable with the natural period of the atomic electrons. It follows from the above values that in the branch collisions dealt with here the effect of binding forces is negligible even for the most firmly bound electrons in the atoms traversed. The electrons may accordingly be treated as free and the expression (1) for ϕ (Q) is applicable.

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* 'Roy. Soc. Proc.,' A, vol. 125, p. 420 (1929).

† 'Roy. Soc. Proc.,' A, vol. 126, p. 289 (1930).

‡ Williams, 'Nature,' vol. 119, p. 489 (1927).

In the case of "branching" it is impossible to determine which is the branch track and which the continuation of the primary track. In actual observations the track of less energy is always counted as the branch, and to allow for this (1) must be slightly modified. The maximum energy of such branches cannot exceed half the energy, T, of the primary β-particle before the collision, whilst the number of them (which we shall represent by P (Q)) is evidently obtained by adding to the right-hand side of (1) the number of collisions in which energy T − Q is lost by the β-particle. It follows that

$$\mathrm{P}(\mathrm{Q}) = \phi(\mathrm{Q}) + \phi(\mathrm{T}-\mathrm{Q}), \tag{3}$$

which on classical theory gives

$$\mathrm{P}(\mathrm{Q}) = (2\pi e^4 n/mv^2)/\mathrm{Q}^2 + (2\pi e^4 n/mv^2)/(\mathrm{T}-\mathrm{Q})^2, \tag{3A}$$

It will be observed that when Q is small compared with T − Q the contribution of the extra term is negligible.

The new quantum theory of the collisions between two electric particles leads in general to scattering formulæ which are identical with the classical formulæ, but this is not the case if the particles are of the same kind as in the collisions between two electrons. This is a consequence of the application of Pauli's exclusion principle, which in terms of wave mechanics means that of the various possible solutions of the wave equation for electrons only the antisymmetrical solutions are represented in nature. Pauli's exclusion principle originally referred to the bound electrons in an atom. It was subsequently successfully applied to the conducting electrons in a metal by Sommerfeld, but here again the electrons are effectively bound and possess discrete energies. The application of the principle to collisions, that is to open systems, was first made by Oppenheimer,* and the special case of collisions between free electrons investigated by Mott,† but apart from the present experiments no evidence has yet been brought to bear on the validity of its application in such cases.

The exclusion principle requires the wave function representing colliding electrons to be antisymmetrical when all co-ordinates are taken into account,

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* 'Phys. Rev.,' vol. 32, p. 361 (1928).

† 'Roy. Soc. Proc.,' A, vol. 126, p. 259 (1930).

i.e., the spin co-ordinates as well as the co-ordinates of position. If the latter only are considered symmetrical and antisymmetrical solutions are possible, but they have different weights in the ratio of 3 to 1. These considerations led Oppenheimer to the following result for the intensity of the stream of electrons which leave in a direction θ with respect to the incident stream, as the result of interaction between the β-particles and atomic electrons

$$\mathrm{I}_q(\theta) = \tfrac{1}{4}\,|f(\theta) + g(\theta)|^2 + \tfrac{3}{4}\,|f(\theta) - g(\theta)|^2, \tag{4}$$

where $f(\theta_1)$ and $g(\theta_2)$ form an unsymmetrical solution of the wave equation, $f(\theta_1)$ representing scattered electrons (or β-particles) and $g(\theta_2)$ the corresponding recoil electrons from the atoms.

For the collisions between β-particles and *free* electrons $|f(\theta)|^2$ and $|g(\theta)|^2$ are respectively identical with the classical intensities of the scattered β-particles and recoiling electrons. Since for every β-particle scattered through θ an electron recoils in the direction $\pi/2 - \theta$ we also have for free electrons $|g(\pi/2 - \theta)| = |f(\theta)|$. There is a phase difference between the "scattered de Broglie waves" represented by $f(\theta)$ and the "recoiling waves" represented by $g(\theta)$.* This phase difference is less the greater the velocity of the incident β-particles, being of the order of $c/137v$, where c is the velocity of light. For the β-particles dealt with here $c/v \sim 4$ so that the phase difference is negligible. For such particles we therefore obtain, by substituting $\phi(\theta)$ for $|f(\theta)|^2$ in equation (4), where $\phi(\theta)$ is the classical intensity of scattered β-particles,

$$\mathrm{I}_q(\theta) = \phi(\theta) + \phi(\pi/2 - \theta) - \sqrt{\phi(\theta)\,\phi(\pi/2 - \theta)}. \tag{4A}$$

This result of the application of (4) to collisions with free electrons was first given by Mott,† and (4A) is the special case for moderately fast β-particles ($v \gg c/137$) of the general formula obtained by him.

The frequency of branches corresponding to (4A) is

$$\mathrm{P}_q(\mathrm{Q}) = \phi(\mathrm{Q}) + \phi(\mathrm{T} - \mathrm{Q}) - \sqrt{\phi(\mathrm{Q})\,\phi(\mathrm{T} - \mathrm{Q})}. \tag{4B}$$

Its ratio to the classical value represented by (3) is given by

$$\mathrm{P}_q(\mathrm{Q})/\mathrm{P}_{\mathrm{cl.}}(\mathrm{Q}) = 1 - \sqrt{\phi(\mathrm{Q})\,\phi(\mathrm{T} - \mathrm{Q})}/\sqrt{\phi(\mathrm{Q}) + \phi(\mathrm{T} - \mathrm{Q})}. \tag{6}$$

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* The terms within inverted commas refer to the unsymmetrical solution. In the symmetrical or antisymmetrical solutions there is no distinction between scattered and recoiling waves (which must be the case for any solution which gives no more information than can be found experimentally, see Mott, 'Roy. Soc. Proc.,' A, vol. 125, p. 222 (1929)).

† 'Roy. Soc. Proc.,' A, vol. 126, p. 257 (1930).

For $Q = T/2$ (scattering through 45°) the value of this ratio is 1/2. As Q decreases $\phi(Q)$ increases rapidly and the ratio approaches unity with decreasing Q. In other words the number of short branches is the same on the two theories whilst the number of the largest branches according to the quantum theory is only one-half the classical number. It might be pointed out that if the exclusion principle were ignored and two colliding electrons treated as distinguishable particles the quantum formulæ would be identical with the classical formulæ, $I_q(\theta)$ being represented by $|f(\theta)|^2 + |g(\theta)|^2$, *i.e.*, by $\phi(\theta) + \phi(\pi/2 - \theta)$ and $P_q(\theta)$ by (3), *i.e.*, by $\phi(Q) + \phi(T - Q)$.

Both the quantum formula (4) and the classical formula (3) are based on the assumption that in "branch" collisions the atomic electrons may be treated as free. We have shown that this is fully justified in the classical calculations and though in general effects which may be neglected in classical calculations may also be neglected in quantum calculations it is not always so. In fact, we shall see that in the present case there is a certain amount of experimental evidence that the nucleus plays a part in the collisions which give rise to small branches, so that for such branches formula (4) may not adequately represent the requirements of quantum theory.

§ 2*b*. *Observations.*

Observations on the frequency of branches by the Wilson cloud method consist in determining the number and energy of the branches produced by β-particles of known velocity in travelling a given distance. The β-particles dealt with here are photoelectrons produced by homogeneous X-rays reflected from a crystal. The observations were limited to the initial portions of the tracks for which the mean velocity was determined with sufficient accuracy from the initial velocity of the β-particle, the latter being accurately known from the wave-length of the X-rays.

The energy of the branches was determined from their ranges. For this purpose it is necessary to know the relation between the initial energy of a β-particle and its range in the region of energies concerned. J. M. Nuttall and the writer* made observations some time ago on the ranges of β-particles with different initial energies in different gases, about 20 "tracks" being measured in each case. The writer subsequently measured the ranges in oxygen and nitrogen of 300 β-particles with initial energy of about 20,000 volts and the ranges of a 100 β-particles with initial energy of about 7000 volts, the exact initial energy being known in each case. The "direct" ranges from the origins to the ends of the tracks were also measured in addition to the ranges measured along the paths of the particles (path-range). The results of these observations were used in determining the energy of the branches from their range. In the case of very short branches the range along the path cannot be reliably measured and the energies of such branches was determined by measuring their direct ranges and converting these into energies by means of the data obtained for direct ranges. This procedure is more reliable and much quicker than to attempt to measure the path-range and use the corresponding data. It might be mentioned that the only objection to the general use of direct ranges in determining the energy of a β-particle is that errors due to "straggling" are somewhat greater than when path-ranges are used. Whichever procedure is adopted the error due to straggling predominates over other sources of error. If path-ranges are dealt with then for individual particles the probable error in the energy from this source (computed from the observed relation between energy and *average* range) is about 10 per cent. In the present observations the number of branches dealt with is such that the straggling error is reduced to a few per cent.*

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* 'Phil. Mag.,' vol. 2, p. 1109 (1926).

Observations were made on the branches produced by about 1100 β-particles, with energy of about 20,000 volts, which corresponds to a velocity of about one-quarter that of light. The total length of track examined was about 400 cm., which yielded about 150 branches. The results are given in the following table.

Table I.—Number of Branches produced by β-particles with 20,000 volts energy in Nitrogen and Oxygen.

Energy of branch-electron. (Volts.)	Observed number of branches.	Theoretical number according to classical theory.	Ratio of observed number to classical number.	Ratio of number according to quantum theory to classical number.
3000–5000	89	100	0·89 ±0·10	0·78
5000–10000	47	78	0·60 ±0·07	0·59

The observations included branches with energies as small as 2000 volts but a large number of such short branches probably escaped detection and only branches with energy greater than 3000 volts are included in the table.

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* The systematic error due to straggling is negligible.

The results show that the classical theory roughly represents the observed frequency of branches. The differences are, however, outside experimental error, the number of collisions in which the β-particle loses between one-quarter and two-thirds of its own energy being only a little over one-half of the classical value. For lighter collisions the observed number approaches that required by the classical theory. As shown at the end of § 2*a* this is precisely the state of affairs required by the new quantum theory. The actual values of the ratio of the numbers required by the quantum theory to the classical number (represented by (6)) are given in the last column of the table. It is seen that the differences between these values and those in the fourth column, which represent the ratio of the observed numbers to the classical numbers are within the experimental error. As far as they go the experimental results therefore provide evidence in support of the new quantum theory and in particular of the extension of the exclusion principle to aperiodic, or open, systems.

It should be mentioned that of the two regions of Q for which comparisons are made in Table I the results for the larger values of Q are the more reliable. One reason for this is that there is evidence (see § 3) that for small values of Q (in the neighbourhood of 4000 volts) some of the observed collisions may not be collisions with a free electron but may also involve the nucleus. To compare with the quantum formula (4B) (which assumes free electrons) these collisions must be subtracted from the observed values given in Table I. However, as the observed values of P (Q), for small values of Q which are given in the table, are greater than the theoretical values the necessary reduction would probably not introduce any serious discrepancy between theory and experiment.

As mentioned in the introduction, observations on the frequency of branches were also made by C. T. R. Wilson. Wilson observed the number of branches produced in air by β-particles with nearly the same energy as those dealt with here. He found in one set of observations that the number of branches with a range at normal pressure greater than $\frac{1}{4}$ mm., produced per centimetre of path is 0·25. According to the results of the above-mentioned observations on the relation of range to energy, a range of $\frac{1}{4}$ mm. in air corresponds to 2800 volts. The classical number of branches per centimetre with energy greater than 2800 volts is 0·33, so that the ratio of observed to classical $= 0\cdot25/0\cdot33 = 0\cdot74$. This agrees satisfactorily with the present results for the number of branches with energy greater than 3000 volts, which is $136/178 = 0\cdot76$ of the classical number. Wilson made other observations but these involve greater experimental error and give inconclusive results.

§ 3. *Energy and Momentum Relations in Branch Collisions.*

Observations on the energy relations were made in the case of collisions in which β-particles with energy of about 16,000 volts produce branches with energy of about 4000 volts in oxygen and nitrogen. The initial energy of the β-particles was known from the wave-length of the X-rays producing them and the energy just before the branch collision was obtained by measuring the distance travelled from the origin and applying empirical laws for the rate of loss of energy. The energies of the branch electron and the β-particle after the collision were obtained from their ranges. Allowance was made for the binding energy of the branch electron. Owing to the appreciable straggling of the ranges of β-particles measurements on single collisions are inconclusive and in the present work observations were made on 45 collisions. The following is a statement of the mean results for these collisions.

Table II.

(Energy expressed in kilovolts.)

Energy of β-particle before collision	$16\cdot2 \pm 0\cdot25$	
Energy of longer fork after collision, neglecting binding energy	$12\cdot4 \pm 0\cdot2$	$16\cdot75 \pm 0\cdot3$
Energy of shorter fork after collision, neglecting binding energy	$4\cdot2 \pm 0\cdot2$	
Binding energy	$0\cdot15$	
Total energy of β-particle and branch electron after collision	$16\cdot75 \pm 0\cdot3$	

It is seen that within experimental error the energy after the collision is the same as the energy before. Regarding the shorter fork as the branch we may say that the energy of the branch electron is $4\cdot3_5 \pm 0\cdot2$ kilovolts whilst the observed loss of energy by the β-particle is $3\cdot8 \pm 0\cdot3$ kilovolts.

No quantitative observations were made on the momentum relations in branch collisions since the considerable scattering prevented reliable measurements of the angles to be made. C. T. R. Wilson* in 1923 investigated the momentum relations, his observations being made on branches with energy of about 4000 volts produced in air by β-particles with about 20,000 volts energy. Wilson found that in about 30 per cent. of such collisions the deflection of the β-particle is much less than that which corresponds to the momentum of the branch electron. If we suppose that the change in energy is equal to the energy of the branch electron in these cases, then to obey the conservation of energy and momentum we must assume that in these collisions a third body must play a part. This third body must have considerable mass so that it may take up momentum without acquiring appreciable energy. Such a body is the nucleus. It is, however, impossible to account for the results if we assume that the effect of the nucleus is given by classical theory. In the first place, the classical effect of the nucleus is too small to influence the deflection of the β-particle appreciably; for in branch collisions, as shown at the beginning of the paper, the distance of approach of the β-particle and atomic electron is only 1/50th of the electron-nucleus distance for the innermost electrons of oxygen and nitrogen. It follows that the β-particle cannot pass near enough to the nucleus to be appreciably deflected by it, and at the same time pass close enough to an atomic electron to produce a branch. In the second place, nuclear deflections even if large enough would not systematically oppose deflections produced by the branch electron, and they would be expected to enhance the latter as often as reduce them. The action of the nucleus in the collisions concerned is thus not intelligible on classical theory and is probably akin to its action when an atom absorbs a quantum in the photoelectric effect; in which case the electron acquires practically all the energy and the nucleus balances the momentum. A classification of collisions into two classes corresponding respectively to the photoelectric and "Compton" collisions of photons with atoms was recently proposed by the writer,* and it is hoped shortly to make further observations on the energy and momentum relations in branch collision to test the points at issue.

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* *Loc. cit.*

Before concluding it should be observed that the quantum theory calculations of the frequency of branches, the requirement of which are represented in Table I, are made for the collisions between two free electrons. They, therefore, do not refer to the branch collisions in which the deflection of the β-particle does not correspond to the momentum of the branch. These considerations do not affect the comparison made in Table I in the case of the branches with large energy, for which there is no evidence that the β-particle is not adequately deflected in the corresponding collisions. Conclusions as to the validity of the quantum formula for the frequency of branches of small energy, *i.e.*, small angles of scattering, must, however, be reserved until further observations are made.

Summary.

Observations have been made on the frequency of production of branches by 20,000-volt β-particles in oxygen and nitrogen. Classical theory only gives the order of magnitude of the number of branches whilst the quantum

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* 'Roy. Soc. Proc.,' A, vol. 125, p. 443 (1929).

theory agrees with the experiments within experimental error. Observations on the energy relations show that in a branch collision the β-particle loses energy equal within experimental error (15 per cent.) to that acquired by the branch electron.

In conclusion I should like to thank Prof. W. L. Bragg for his kind interest in the above work.

On the Stability of Unimolecular Films. Part IV.—*Amines.*

By C. G. Lyons and Eric K. Rideal, Laboratory of Physical Chemistry, Cambridge.

(Communicated by Sir William Hardy, F.R.S.—Received May 7, 1930.)

In the earlier papers of this series it was concluded that both in solid films and in films in the smectic or liquid condensed state, the chain axes were not vertically inclined to the surface of the substrate. Solid films were regarded as comparable with crystals and their stability was attributed to the interlocking of the zigzags of the hydrocarbon chains. On this view, the area of simple aliphatic molecules should possess in the solid condensed state certain unique values, viz., 18·6 Å., 20·5 Å., 26·2 Å., corresponding to an interlocking in the vertical state and in the first and second zigzags respectively. The highly tilted state of area 33·7 Å. corresponding to the third zigzag would naturally be extremely unstable. Since the polar heads are generally asymmetrically attached to the chain axis, the vertical form is not found. A number of cases of solid films with areas determined by the first coincidence of the zigzags were cited in the earlier papers. It was pointed out that the monoglycerides examined by Adam might be examples of the second coincidence. The ureas (likewise examined by Adam*) of areas 20·6 and 26·2 Å. per molecule were regarded by us as a definite case of two dimensional dimorphism,† with molecules tilted to the first and second coincidence of the zigzags respectively. We obtained an area of 26·2 Å. per molecule for a long chain amine in the solid state as a case of second coincidence,‡ but Adam§ (working chiefly with an amine hydrochloride on substrates of different composition to ours) obtained solid films of area 20·5 sq. Å. per molecule, *i.e.*, in the first coincidence. It was important to establish another definite case of a solid film in the second coincidence and to investigate the possible existence of another case of dimorphism in thin films. The fresh work described in this paper was undertaken to discover the cause of the discrepancy in the experimental results of Adam and ourselves.

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* 'Roy. Soc. Proc.,' A, vol. 101, p. 452 (1922).

† Lyons and Rideal, 'Nature,' vol. 125, p. 455 (1930).

‡ Lyons and Rideal, 'Roy. Soc. Proc.,' A, vol. 124, p. 322 (1929).

§ 'Roy. Soc. Proc.,' A, vol. 126, p. 526 (1930).

The present work has confirmed that published previously and has also extended it considerably ; the different results obtained by Adam have been shown to be due to the different conditions under which he worked and we have been able to confirm his results under these conditions.

Experimental.

The apparatus and technique have been described already (*loc. cit.*). The earlier experiments had been carried out with the free base alone, but most of Adam's results were obtained with their salts. Therefore in the present experiments both normal heptadecylamine and octadecylamine hydrochloride were used. The former substance was dissolved in petroleum ether (B.P. 67° C. to 70° C.), while a mixture of absolute alcohol (20 per cent.) and petroleum ether served as a solvent for the latter substance.

The heptadecylamine was a specimen freshly obtained from Messrs. Siegfried of Zürich, and was specially purified for us by Mr. A. S. C. Lawrence, to whom we express our thanks. The purification was effected by boiling with strong aqueous potash and distilling *in vacuo* from quicklime. The heptadecylamine then melted at 48° to 49° C.

The octadecylamine hydrochloride was kindly supplied by Dr. N. K. Adam, and was used unchanged.

The buffer solutions were made up according to the directions given by Clark (" The Determination of Hydrogen Ions ").

The force/area curves of these substances were determined in the usual way, attention being directed primarily to the condensed states and particularly the solid films. The curves obtained were of the usual form showing solid condensed, liquid condensed, and sometimes expanded portions.

It was found that the free base and the hydrochloride often behaved quite differently, in a manner which sufficed to explain the discrepancy between Adam and ourselves ; and Adam's failure to detect this difference must be due to an accidental choice of conditions. Unfortunately, he does not give details of any experiments with the free bases; but as far as can be seen our results are not in disagreement with his.

Experiments with Heptadecylamine.

It was found that the area of the solid condensed films of this substance depended on the temperature. Above a certain temperature a solid film of area 26·2 sq. Å.U. per molecule was obtained, and below a lower temperature the solid film had an area of 20·5 sq. Å.U. per molecule. The temperature interval between these regions was very narrow (3° to 4° C.).

This phenomenon must be compared with the dimorphism of the ureas.* The behaviour of the amine differs from that of the ureas only in that the form with the larger area is stable at the higher instead of the lower temperature. It is on this account that this dimorphism was not noticed in the earlier work, since the search for the smaller area form was then made by raising instead of lowering the temperature.

The transition temperature was slightly lower on the more alkaline solutions, so that when a series of solutions of varying alkalinity were examined, the change from the larger to the smaller area took place at constant temperature over a range of P_H. This is illustrated in fig. 1, while fig. 2 shows the transition taking place over a narrow temperature range for two different solutions.

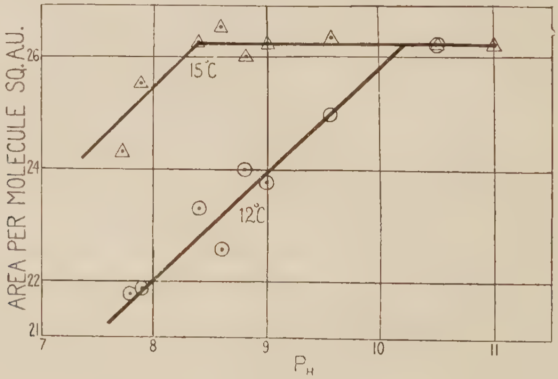

FIG. 1.

Films on solutions on the acidic side of neutrality collapsed too readily to be used to extend the curves in that direction.

The measurements described in our previous communication were all made at 15° C. and over,† and the form with the larger area was therefore stable on all the solutions examined. These new results therefore confirm the older ones. (There is only one discrepancy, the earlier curves showing an area of 26·2 sq. Å.U. per molecule on P_H 7·3. This difference corresponds to an error in the temperature measurement of 1° C., 16° C. instead of 15° C.)

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* P. 468.

† There is a misprint on p. 338, line 12, Part II, where 5° C. should read 15° C.

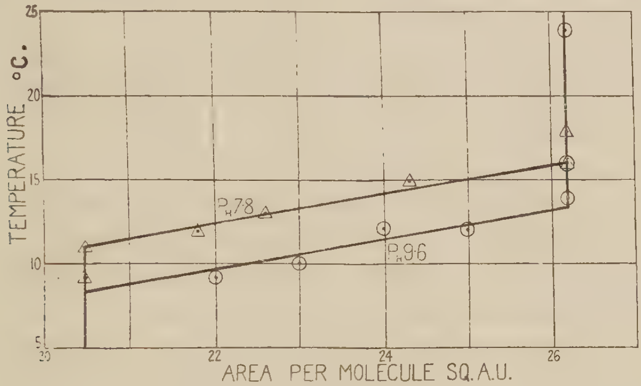

Fig. 2.

Experiments with Octadecylamine Hydrochloride.

On very alkaline solutions and on almost neutral solutions the solid condensed films of this substance have areas of 20·5 sq. Å.U. per molecule. These values are identical with those of Adam, but are not the same as those given by the free base. On borate solutions of an intermediate alkalinity (P_H 8·8–9·6) the hydrochloride forms films with areas identical with those of the free base, *i.e.*, values between 20·5 and 26·2 sq. Å.U. per molecule depending on the temperature. This surprising observation had been overlooked by Adam since he did not work between the necessary limits.

There is one minor difference between our results and those of Adam for films on phosphate buffers. He found that while the amine gave a film of about 26 sq. Å.U. per molecule on M/20 and M/1000 solutions, the hydrochloride gave 20·5 sq. Å.U. per molecule only on the M/1000 solutions. We found that the hydrochloride gave 20·5 sq. Å.U. per molecule on both solutions, the free base giving 26·2 sq. Å.U. All these films were found to be solid; and the areas agreed within experimental error with the areas calculated for interlocking chains.*

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* Adam has overlooked the existence of these areas or the solidity of these films in summarising his results with reference to the hypothesis of interlocking chains.

Discussion.

These experiments establish the existence of two stable solid films given by the amines and their salts. It seems very probable that the change between the two different solid films is analogous to a true transition between two crystal forms in three dimensions. In the films the two " crystal " types consist of molecules tilted till the chains interlock after displacements of one and two zigzags respectively, and the experimental areas agree well with those calculated for molecules in these positions. The narrowness of the transition interval is strong evidence in favour of this analogy with bulk matter ; although in that case the transition is absolutely sharp. It is probable that when the two forms become of nearly equal stability, the film " crystallises " as a mixture of the two types. This is supported by the observation that the intermediate areas are slightly less reproducible than the two areas.

The problem of the causation of the different tilts is still indefinite. In the case of the ureas it was suggested that the head group may exist in two forms with different asymmetries. The amines and their salts have several different forms of head group, each of which will have a different angle of free tilt. The fact that increased alkalinity favours the larger area form suggests that this form may be due to the free base, and not a salt. But it is possible that some salts of the amines may have sufficiently asymmetric head groups to give solid films with this area. The area of 26·2 sq. Å.U. per molecule on phosphate buffers at P_H 7·0 may be due to the amine phosphate. Also we have observed that this form is obtained on strong carbonate solutions, whence it may follow that the amine carbonate has a highly asymmetric headgroup.

The apparently capricious behaviour of the hydrochloride remains to be explained. This substance always gave solid films of area 20·5 sq. Å.U. per molecule, except on borate buffers of P_H 8·8–9·6. This area seems to be characteristic of the substance itself. It was observed that a film left on a fairly alkaline solution (P_H 10) gradually increased in area, at constant pressure, while remaining solid. As the hydrochloride became converted into the free base it took up the area characteristic of that substance. This expansion phenomenon has been observed many times. It may be facilitated by permitting the expansion and ionic diffusion to take place when the film is subjected to quite low pressure. In each case the expansion finished as a solid film with an area of about 26 sq. Å.U. per molecule, although it was not possible to determine this final area very accurately.

On the solutions P_H 8·8–9·6, the hydrochloride seems to be converted into free base instantaneously.

The slow expansion undergone by the salt and also by the free base on distilled water must be of a similar nature; perhaps in this case the final highly asymmetric group is the hydrated amino group RNH_3OH.

These conversions of a solid film of area 20·5 sq. Å.U. per molecule into one of area 26·2 sq. Å.U. per molecule definitely establishes the validity of that larger area, and justifies its use for testing the hypothesis of interlocking chains.

Summary.

A further study has been made of the properties of films of the long chain amines. Two stable solid films of areas 20·5 and 26·2 sq. Å.U. per molecule have been found, with a definite transition temperature, thus exhibiting the phenomenon of two-dimensional dimorphism. The hydrochlorides do not always give areas identical with those of the free base. These results extend those previously published by Adam and ourselves and provide additional support for the hypothesis of interlocking chains as a factor in the stability of solid crystalline unimolecular films.

Triboelectricity and Friction.—V. On Surface Strain and Relaxation of Like Solids.

By Prof. P. E. Shaw, M.A., D.Sc., and R. F. Hanstock, B.Sc., University College, Nottingham.

(Communicated by Sir William Hardy, F.R.S.—Received May 6, 1930.)

It has been shown* that the position of a solid, in the triboelectric series, depends on the previous treatment of its surface: thus, ebonite when rubbed by hard solids is lowered in the series; on heating it is raised again. This reversible process holds good, it was shown, for a great number of metals and non-metals.

Later it was demonstrated† that charges arise when two identical surfaces of, say, clean annealed ebonite are rubbed together. Each surface becomes charged and, as rubbing continues, the charges change in amount, and even in sign, in a systematic way. The effects were attributed to progressive strain on the surface, brought about by pressure and friction. In the present paper we endeavour to standardise these effects by measuring the charges arising between known areas, pressed together by known forces, at stated temperatures.

The apparatus used is similar to that described in a former paper of this series.‡ A rough scheme of the essentials is shown in fig. 1. A wooden

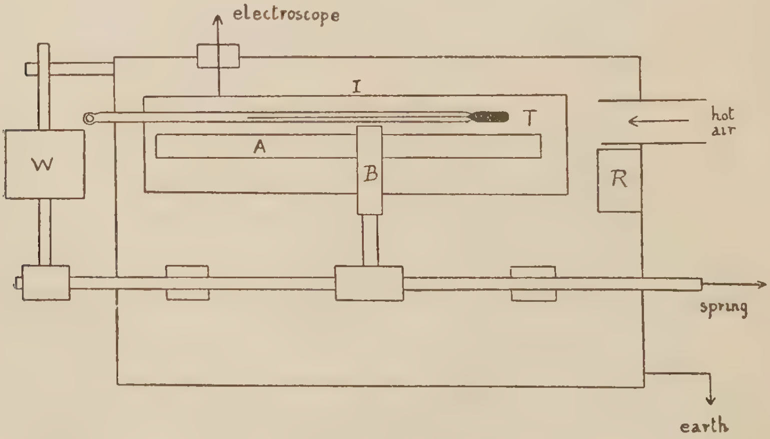

Fig. 1.—Apparatus.

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* Shaw, 'Roy. Soc. Proc.,' A, vol. 94 (1917).

† Shaw, 'Proc. Phys. Soc.,' vol. 39, p. 449 (1927).

‡ Shaw and Jex, 'Roy. Soc. Proc.,' A, vol. 118, p. 97 (1928).

chamber lined with metal is closed on all sides. Of the two rods on which the experiment is to be made, the first, A, called the "rubbed" rod is fixed, insulated, and partly surrounded by a metal plate, the inductor *I* which, itself insulated, is joined to an electroscope. The second, movable, rod B, called the "rubber," is pressed by a lever with known weight, W, on the first rod and made to slide a known distance along A, and then removed. The charge produced by rubbing induces a charge on the inductor, and hence charges the electroscope. If desired the rods are then discharged by opening in the chamber a lead box, R, containing radium.

We use such a symbol as ebonite-ebonite to imply that of the two ebonite rods the first is movable, the second fixed, and that the charge found is that on the second. In the present research we have effected improvements, the principal one consisting in maintaining the air in the rubbing apparatus dry and constant in temperature. This is important, for it has been demonstrated by Vieweg,* and others, that adsorbed moisture in the rubbing surfaces may mask, or even change the sign of, the true charge. We therefore maintain the working temperature about 50° C. and relative humidity below 25 per cent. We find the results consistent under all atmospheric conditions; and by this method of working avoid the great difficulties involved in working the mechanism in *vacuo*. Hot air is supplied to the chamber by a fan motor, the air from which passes through a heating coil. In this way any temperature from 50° C. to 110° C. can be maintained indefinitely in the chamber. For lower temperatures the air passes through drying tubes before passing the heating coils.

The materials used are ebonite, celluloid, silk, zinc, copper, cadmium, tin and iron. We wish to thank Mr. A. Healey, B.Sc., Research Manager, Messrs. Dunlop Rubber Company, Erdington, for a supply of high-grade ebonite rods, which have proved much more consistent than some commercial ebonites, To prepare ebonite and celluloid rods for use, they are scraped to remove polish, then annealed in boiling water for, say, 20 minutes (longer for poor quality ebonite); and allowed to dry and cool. The metal rods are prepared by scraping with a clean blade, and then annealing in a heating coil: to 300° for iron and copper: to 200° for tin, cadmium and aluminium.

In some experiments the surfaces are strained before use. This is achieved by rubbing together two clean rods of the same material, one being spun between centres in a lathe. The method of working the apparatus described above is as follows: One rub is made, the charge read, and the rods discharged.

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* 'J. Phys. Chem.,' vol. 30, p. 7 (1865).

Another rub is then made, the effect noted and obliterated as before, and so on. Any change in the physical condition of the rods caused by friction is shown by the alteration of charge.

Results.

I. *Ebonite-Ebonite.*—The curve for 30°, fig. 2, begins at about + 5 volts, which potential decreases in 150 rubs to zero, and the curve then just crosses the line to negative potential, reaching approximately the limiting value. As temperature is raised in the apparatus the curves open out at both ends, and the zero point is reached earlier. By observation with a microscope it is found that the small circular rubbing area on the *rubber* is to the long area on the *rubbed* rod as 1 : 53.

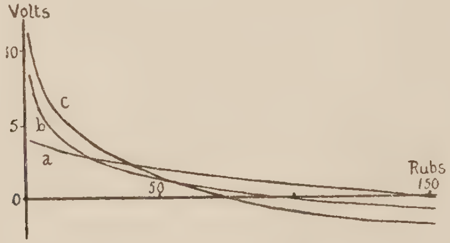

Fig. 2.—Eb.-Eb. (*a*) at 30° C. (*b*) at 75° C. (*c*) at 105° C.

To interpret these results, it is clear that since the energy spent on both rods is identical the small area of the rubber surface is more heated and strained than the larger area of the rubbed surface. These surfaces are alike at first, but on rubbing become physically different and the difference is shown in the electric separation; the charge on the *rubbed*, as the curve shows, being positive, and on the *rubber* negative. At each stroke, the surfaces in action both acquire more heat and more strain, and this goes on as rubbing continues. But as the area of the *rubber* is small, temperature and strain rise more quickly on it than on the larger, rubbed, area. Rise of temperature, as we shall see later, engenders recovery from strain; the result being that the rubber soon attains to a limiting temperature and strain. The *rubbed* does not rise much in temperature, as the work done on it is spread over a large area. It is a "cold-worked" surface, so that strain increases steadily and finally exceeds that on the *rubber*. We shall prove that strain renders ebonite negative in action, and this being so we see how the charges commence negative for the *rubber* and end negative for the rubbed rod. For the higher temperature curves strain differences would be more speedily attained. Fig. 3 represents an experiment in which one or other ebonite (but not both) is initially strained to the limit, as explained earlier. Curve *a* represents the case when the rubbed body begins strained; in curve *b* the *rubber* begins strained. Curve *c* is the normal case when neither rod commences strained.

In figs. 4 and 5 we see how strain is relaxed by lapse of time, or by rise of temperature as seen by the charges produced. In fig. 4 commercial ebonite is used. At 90° there is no recovery for pauses of 5 minutes; even at 112° the recovery after 5 or 20 minutes is small. But in fig. 5 for pure ebonite, though the working temperature is only 60° relaxation is pronounced. In the *a* curves the interval between each rub is 1, 30, 60, 120 seconds in the four cases; the curves for the shorter times suggest that relaxation proceeds according to the usual relation, $S = S_0 . e^{-zt}$, where S = strain, t = time, z = constant, S_0 = initial strain. In curves *b* and *c* a new method is adopted, one rod only being progressively strained. In *b*, the *rubbed* rod is turned after

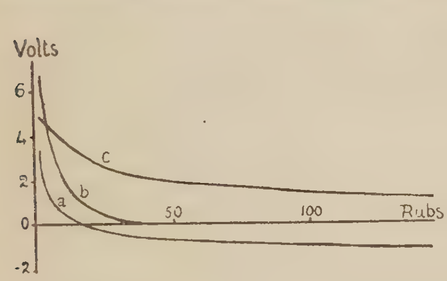

Fig. 3.—Eb.-Eb. at 30° C.
(*a*) Rubbed. (*b*) Rubber. (*c*) Normal.

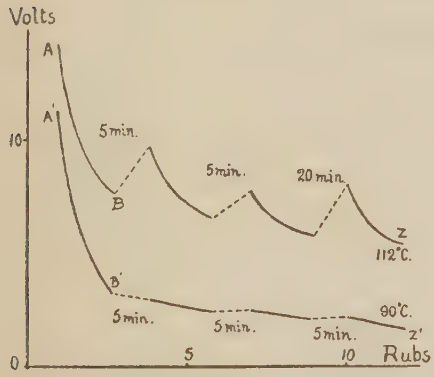

Fig. 4.—Relaxation of Ebonite.

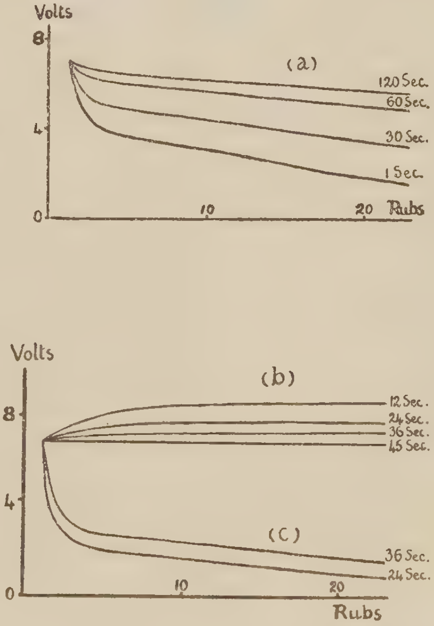

Fig. 5.—Eb.-Eb. at 60° C. Spontaneous Relaxation.

each rub, so as to present always a fresh surface; thus the strain progresses only on the *rubber* and the strain on the *rubbed* steadily increases. In *c* the *rubber* is turned after each stroke, so that the relative strain on the *rubbed* grows very quickly, as the steep drop of the curves show.

To sum up: the results shown in figs. 2, 3, 4 and 5 for ebonite establish three principles: (1) charges on like materials are due to differential strain, (2) the more strained surface is the more negative, (3) spontaneous relaxation occurs, especially in pure material. This last point suggests, as a matter of technique, that in order to have results made under various conditions comparable it is necessary to have the time interval between rubs constant.

II. *Celluloid-Celluloid.*—Fig. 6 shows results for this material, the process being that described for ebonite (fig. 2), and as the curves are of the same nature in the two cases, the inference is that at least as regards principles (1) and (2) above, celluloid is akin to ebonite, as regards strain and charging. For the present case the rubbing areas are found to have the ratio 1 : 75.

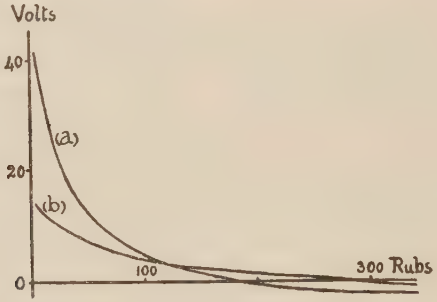

FIG. 6.—Cel.-Cel. (*a*) at 75° C. (*b*) at 23° C.

III.—In our next paper we show similar effects when like metals are rubbed together.

Vacuum Experiments.

The pressure at any point distant r from the centre of the circular area of contact, of radius a, when the applied pressure is W, is by Hertz's equation of deformation:

$$p = 3W(a^2 - r^2)^{\frac{1}{2}}/2\pi a^3.$$

The maximum pressure, when $r = 0$, is therefore

$$p_m = 3W/2\pi a^2 = 100 \text{ atmospheres approximately in our experiment.}$$

Thus, if our rubbing were performed in vacuum instead of in air the reduction in pressure would be only 1 per cent., so that the strain effects would be only imperceptibly different. But there is a possibility that for work in air the adsorbed air films on the surfaces may play an important part in our effects. In a vacuum of, say, $\frac{1}{10}$ mm. these films would surely be absent, any residual film before rubbing commences being removed when the surfaces are agitated by friction. The next step, then, is to repeat the above processes in vacuum, and if we find the results unchanged we shall conclude that air films do not take any part in these strain phenomena. For this purpose a new apparatus is used. Into a glass tube, which can be exhausted, is inserted a framework on which is fixed a rod of ebonite. Another loaded ebonite rod is attached to a slider so that on tilting the glass tube this rod slides over the fixed one. The charge generated on the fixed rod induces contrary charge on an inductor which is connected by insulated wire to an electroscope outside the tube.

The results of four experiments (see fig. 7) are given: one at atmospheric pressure; the others at the pressures shown. The curves are of the same type for all the pressures, the differences between them being attributed to varying contact areas of rubbing.

In fig. 8 are results for silk-silk in vacuum. This material was exhaustively cleansed of natural pectins and other impurities by long treatment.* We observe that as with all the materials already mentioned, silk shows strain effects; and, further, as with them, the charges obtained depend on previous heat treatment. The depression seen in the curves for material recently heated is explainable on the strain theory if we suppose that strain renders silk more positive in action.

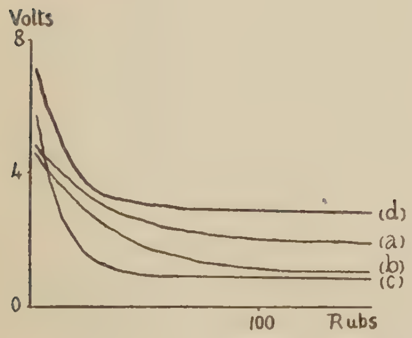

Fig. 7.—Eb.-Eb. at 18° C. Pressure at (*a*) 760 mm. (*b*) 0·7 mm. (*c*) 0·2 mm.

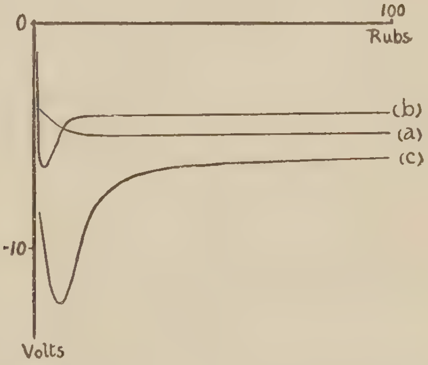

Fig. 8.—Silk-Silk. (*a*) Not heated, 760 mm. (*b*) Heated, 1·0 mm. (*c*) Heated, 0·2 mm.

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* See former paper, Shaw and Jex, 'Roy. Soc. Proc.,' A, vol. 111, p. 346 (1926).

Summary.

1. When two identical non-conductors, whether of ebonite, or celluloid, or silk, are rubbed together, each becomes charged in a systematic way. The charges are attributed to differential strain on the surfaces, caused by the rubbing.

2. Thus we have a new method of investigating surface strain. Also, as the rubbing solids are identical chemically, triboelectric phenomena can be more easily and directly studied than when, as is usually the case, unlike materials are used.

3. Recovery from strain can be completely attained by rise of temperature. Since rubbing necessarily raises temperature locally, strain and partial relaxation from strain proceed simultaneously.

4. Experiments in vacuum give results similar to those in open air; so it is concluded that the effects are entirely due to changes on the solid surfaces; and not, even in part, to the action of films adsorbed on the surfaces.

Triboelectricity and Friction.—VI. *On Surface Strain and Relaxation for Unlike Solids.*

By Prof. P. E. Shaw, M.A., D.Sc., and R. F. Hanstock, B.Sc., University College, Nottingham.

(Communicated by Sir William Hardy, F.R.S.—Received May 6, 1930.)

In the paper preceding this we have dealt with strain effects between like materials, and we now consider the case when the materials are unlike.

The curves for zinc-ebonite (fig. 1) are of the same type as those for ebonite-ebonite (fig. 2 in the last paper) but the charges are now much larger and change sign with fewer rubs. Both these effects are to be expected: the first, because the two materials are chemically different; the second, because zinc is relatively hard and will very quickly develop full strain on the softer ebonite. The ratio of the rubbing areas is 1 : 45.

In fig. 2, curve *a* is for initial strain in zinc only; curve *b* for initial strain in ebonite only; the other material in each case being unstrained. We pause to consider the difference between the rubbing together, as here, of surfaces of unlike composition and hardness and the rubbing, as before, of like surfaces.

In the first place, the metal being hard would be much less strained than the softer ebonite, if the two surfaces rubbing were subject to equal treatment; but they are not. As the ratio of areas shows, zinc is subjected to 45 times more severe treatment than the ebonite; 45 times more work is done on it per unit area; its temperature will rise and may superficially attain temperature of relaxation; so that its strain may easily be of the same order as that on the ebonite. Fig. 2 establishes the soundness of this reasoning, for in curve *a* the ebonite is changed from 40 to — 15, *i.e.*, 55 units; whereas in curve *b* the zinc changes 15 units.

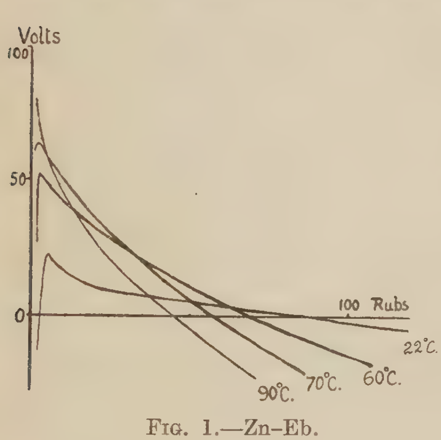

Fig. 1.—Zn-Eb.

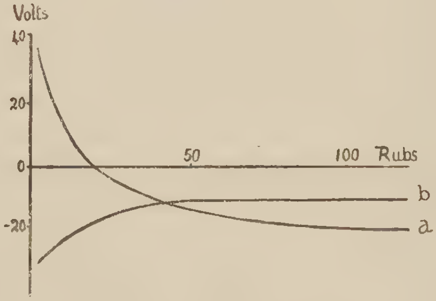

Fig. 2.—Zn-Eb. (*a*) Zn strained.
(*b*) Eb. strained.

Secondly, we must bear in mind that ebonite contains much sulphur, and this may generate sulphides of such a metal as zinc, introducing a new material at the interface. To test this point, a new process is adopted. A metal rod, say zinc, is strained by rubbing it with another zinc rod, instead of with ebonite; and, as rubbing continues, its result is tested by rubbing with annealed ebonite. The results for various metals are seen in fig. 7. For zinc the curve is of the same form as that in fig. 2 where the strain is produced by ebonite. We infer from this that the curves in the latter case, as in the former, are due to genuine strain and not to chemical action of the ebonite on the metal. In fig. 3 are the curves for copper rubbed on ebonite. With comparatively few rubs the copper becomes negative to ebonite. In fig. 4 are curves for copper-ebonite where one of the two materials is fully strained before rubbing commences, the other material commencing annealed. The

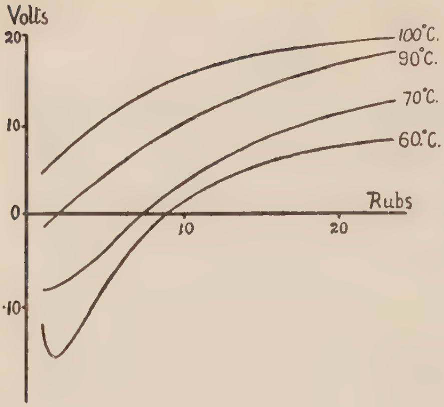

FIG 3.—Cu-Eb.

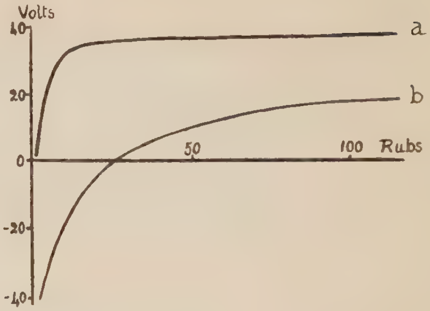

FIG. 4.—Cu-Eb. at 56°. (*a*) Eb. strained.
(*b*) Cu strained.

results are like those for zinc-ebonite (see fig. 2) in showing progressive strain.

In figs. 5 and 6 are curves for tin at 75° C., cadmium at 56° C. and iron at 56° C. Tin behaves like zinc; cadmium like copper; whilst iron is peculiar in showing no tendency for the charge to reverse sign.

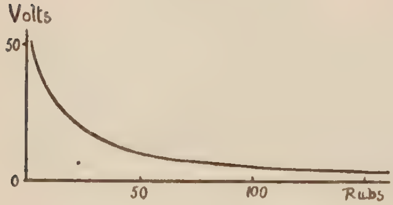

FIG. 5.—Sn-Eb. at 75° C.

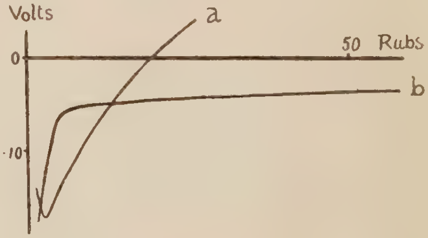

FIG. 6.—(*a*) Cd-Eb. at 56° C.
(*b*) Fe-Eb. at 56° C.

Taking all the curves in conjunction we see that zinc and tin are initially negative; copper, cadmium, and iron positive to ebonite.

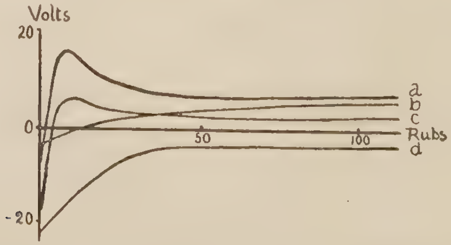

FIG. 7.—(*a*) Eb.-Sn/Sn at 66° C. (*b*) Eb.-Fe/Sn at 66° C.
(*c*) Eb.-Zn/Zn at 66° C. (*d*) Eb.-Cu/Cu at 66° C.

We have referred in the preceding paper to the relaxation temperature of ebonite, which for best quality material is about 100°. In an endeavour to find relaxation temperatures for copper and iron we use fully strained surfaces. These are raised in steps from ordinary temperature to 300° C. After each step the metal is allowed to cool and then rubbed on the annealed ebonite, turning the latter after each rub so that new annealed material is used throughout the experiment. The curves are in fig. 8. Copper begins to relax at 162° C., and iron at 192° C., relaxation proceeding rapidly in both cases at 300° C. It has been stated* that the critical relaxation temperature is about one-third the absolute melting point of the metal. This would be 180° C. for copper and 320° C. for iron. Our values are thus of the right order.

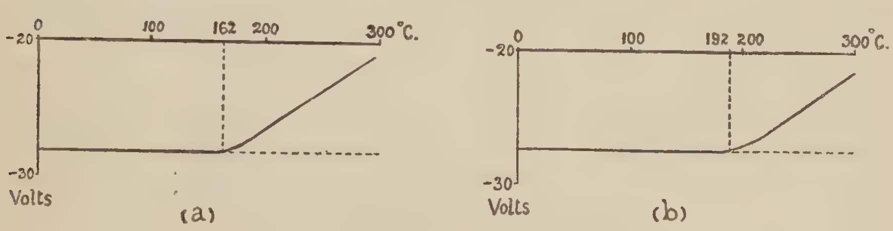

FIG. 8.—Relaxation of Strained Metals.
(*a*) Copper (Cu–Eb.). (*b*) Iron (Fe–Eb.).

The Nature of Surface Strain.

There are certain points of resemblance between surface strain and body strain. If to one solid resting on another, increasing small stress, tangential to the interface, be applied, then before movement occurs, elastic strain arises. The upper solid moves but returns when the stress is withdrawn. This has been shown for sliding friction by Rankin† and for rolling friction by Tomlinson.‡

These effects for the surface correspond to the elastic strain for the whole body of a rod subjected to tension or torsion. Now for permanent or inelastic strain; this, in the case of the whole body of a rod has been extensively studied; but is little understood in the case of surfaces. The researches of Beilby and others on surface flow and polish have not been linked to the modern electrical theory of matter. The problem is to understand the action of individual atoms on the two opposed surfaces. X-ray spectroscopy has failed to discriminate between annealed and strained surfaces even when the rays have glancing incidence. The rays are known to penetrate many layers of atoms, so that any effect on the rays peculiar to a few surface layers would be masked by the much greater effect of those underlying and unstrained.

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* Desch, 'Trans. Faraday Soc.,' vol. 24, p. 57 (1927).

† 'Phil. Mag.,' vol. 2, p. 282 (1926).

‡ 'Phil. Mag.,' vol. 7, p. 905 (1929).

When a rod or wire is cold-worked by being pressed and reduced in diameter between rollers, or through a draw-plate, gliding of crystal planes occurs, many small grains are formed and then both surface and body material become fibrous and hard. On annealing the rod crystallisation occurs throughout body and surface ; but on the surface where a greater degree of freedom exists, *reorientation* of crystal axes also may occur.

Thus by annealing, the organisation of body and surface has become different. Evidence on this point has been given by Thompson and Millington* and by one of us in a preceding paper. If now the surface of the rod be ground by abrasives and polished, it will be reduced to somewhat the same state of strain as before annealing. Now consider the present case of sliding friction. If, say, one copper rod be laid on another, both being annealed, and friction produced between them, we may expect the crystal structure to be disorganised as with rolling or grinding, but in less degree. The degree depends on the force with which the rods are pressed together as we have shown experimentally.

Of the non-metallic materials used by us, silk, like other cellulose material, consists of long chain-like molecules, or crystallites bound by co-valent links into a strong fibrous structure embedded in amorphous material. This is comparable with the fibrous structure found in hard drawn rods of metal. Our other materials, ebonite and celluloid, we take to have no organisation corresponding to that in cellulose. Nevertheless, all these three non-metallic substances, as we have seen, are like the metals in showing progressive strain when rubbed. Thus there appears to be common strain characteristics between all kinds of matter, crystalline and amorphous. But the complications are great.

The complexity of this subject arises from the coarseness of all solid surfaces. Even the best optically true glass or metal surface has roughness of the order of the microscopic limit, say, $\frac{1}{4}$ wave-length, *i.e.*, 5000 atomic lengths. Two such surfaces come into contact in a most haphazard way, and, when pressed together, a great range of elastic and permanent strains arise at the " contact spots," the greater part of the surface being quite out of contact. Frictional and triboelectric effects are due to the fields of surface atoms. If we could work with two ideal surfaces whose atoms lay in mathematical planes, a comprehension of the forms and charges arising would be relatively simple

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* 'Journ. Iron and Steel Inst.,' No. 1 (1924).

Film Effects on Glass and other Surfaces.

An effect sometimes encountered simulates strain. This has been pointed out in previous papers ; its cause we are now able to reveal.

In fig. 9 curves are shown for charges due to glass-silk, both materials being cleansed carefully. The glass starts negative (so the silk has a positive charge as shown) but after 5 rubs it changes sign. The glass is then heated in an electric furnace. At 340° a change occurs, for when cool the glass is again negative. On repetition no change is produced at 200° or 250° ; but at 300° modification occurs. Is the change produced between 300° and 350° a relaxation from strain, or is it a removal of some organic film laid on the glass by the silk ? To settle the point, rods of glass and purest metals are each rubbed first with clean filter paper and the charges on the rods noted. Then the rods are treated with one of a series of pure organic solids of low melting point and are then rubbed with the filter paper, the charges again being observed. To apply the film a rod is turned at speed by a motor and the substance laid on by filter paper. Some materials are easily applied ; in any case the process must continue until only a residual, primary, film is left. In making the test the filmed rod is turned by the motor and the filter paper pressed on it with constant force. The resulting charges are read on a calibrated electroscope. As the Table shows the clean surfaces of glass, ebonite and copper are negative to filter paper ; zinc and iron positive. The introduction of organic films of the materials of the left-hand column change the sign of the charge. in all cases for glass, in several cases for ebonite and metals. We note that for

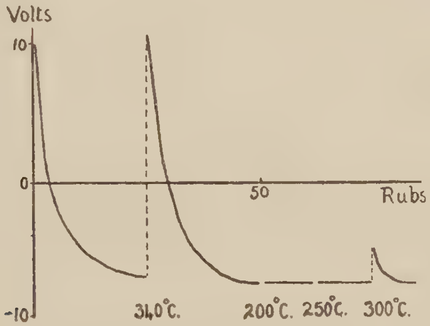

Fig. 9.—Film on Glass (Glass-Silk).

Table.

	Glass (−)	Ebonite (−)	Commercial Cu (−)	Purest Fe (+)	Purest Zn (+)
Felt	+		+		+
Paraffin wax	+	−	+	+	
Palmitic acid	+	+	+	−	−
Lauric acid	+ −	+	+	−	−
Myristic acid	+				+
Stearic acid	+ −				
Succinic acid	+	+			
Malonic aicd	+				
Maleic acid	+				
Benzoic acid	+	+	+		+
Phthalic acid	+				−
Stearic acid	+				+
Ethyl palmitate	+	−			
Ethyl stearate	+	−			
Stearin	+	−	+		

NOTE.—As shown at the head of the columns, glass, ebonite and copper are negative, whereas iron and zinc are positive to filter paper. But by applying to those solids a film of one of the organic materials in the first column, the charges are changed in most cases, but not in all, as shown in the other columns.

ebonite and metals chemical changes occur in many cases (certainly for metals and the acids). Of course all these films are removable by heating the glass or scraping the other rods. These tabular results are only given to demonstrate the danger of accepting results in triboelectricity unless superposed organic films can be proved to be non-existent. The effects for glass-silk mentioned at the head of this section are clearly *due to films* and not to strain. The terminal methyl group of all the organic compounds is on the film surface and acts positive to filter paper. In fig. 10 four curves are shown for soda glass.

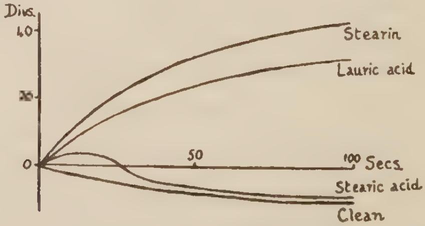

FIG. 10.—Filter paper—Filmed Glass.

The lowest is for filter-paper with clean glass, the others for films. Stearic acid gives a positive film but this appears to be removed by long rubbing so that the original glass surface is exposed and rubs negative. Stearin and lauric acid render the glass surface positive.

Summary.

1. As in the preceding paper strain effects caused by rubbing solids together are studied by the charges arising on the solids. In this paper metals are rubbed with ebonite, or with like metals.

2. Relaxation temperatures are found for surface strain on copper and iron.

3. An effect which simulates strain, inasmuch as the triboelectric state of a solid surface is changed by the process of rubbing it with a fabric, is shown to be due to the deposition on the surface of organic films derived from the fabric. These recall the " primary " films used by Sir Wm. Hardy in researches on boundary lubrication.

4. Frictional electricity is a subject which has long baffled investigation. Surface strain and imposed organic films are two complicating factors. It is clear now that it is possible to minimise the first factor by carrying strain to the limit, and to avoid the second by avoiding fabrics and other doubtful organic bodies. These two troubles being eliminated the course of the experimenter should be clearer.

The Operational Wave Equation and the Zeeman Effect.

By G. Temple, Ph.D., 1851 Exhibition Research Student, Trinity College, Cambridge.

(Communicated by Sir Arthur Eddington, F.R.S.—Received May 23, 1930.)

§ 1. *Introduction.*

The object of this paper is to develop the theory of the Zeeman effect from the operational wave equation

$$W\psi \equiv \{(\mathbf{p} + ec^{-1}\mathbf{G})\,\mathbf{A} + c^{-1}(p_0 + eV)\,\iota A_4 + \iota m_0 c\}\,\psi = 0, \qquad (1.1)$$

V being the electrostatic potential of the nucleus and **G** the electromagnetic potential of the applied magnetic field. The same notation is employed as in a previous paper,[*] viz., the components of **p** are the momentum operators p_1, p_2, p_3; p_0 is the energy operator; A_1, A_2, A_3, A_4 are wave operators, the first three being treated as the components of a vector **A**.

It has been shown[*] that the energy levels of hydrogen-like atoms can be determined from the operational wave equation without making any restrictions on the wave operators other than Dirac's conditions

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[*] 'Roy. Soc. Proc.,' A, vol. 127, p. 349 (1930).

$$\tfrac{1}{2}(A_m A_n + A_n A_m) = \begin{cases} 0 & \text{if} \quad m \neq n, \\ 1 & \text{if} \quad m = n. \end{cases}$$

The study of the Zeeman effect can be pursued in the same agnostic spirit, but although nothing more is assumed with regard to the structure of the wave operators, it now becomes necessary to correlate them with various physical concepts. This necessity arises from the fact that the changes in the energy levels produced by a magnetic field depend upon the magnetic moment of the atom, and this in turn upon the distribution of currents in the atom. Hence the first requisite is the appropriate mathematical expression for these quantities in terms of the wave operators.

The microscopic properties of the atom, *i.e.*, its charge and current density at any point are determined by tensors with components of the form $(T\psi, \phi)$. The possible forms of such tensors and their physical interpretation are studied in §§ 2 and 3. The macroscopic properties of the atom, *i.e.*, its electric and magnetic moments, are determined by integrated expressions of the form

$$[T\psi, \phi] = \int (T\psi, \phi)\, dx_1\, dx_2\, dx_3, \tag{1.2}$$

i.e., upon the "matrix elements" of some operator T. The general principles available for the calculation of these expressions are studied in §§ 4–7 and the special matrix elements required in the theory of the Zeeman effect are determined in §§ 8 and 9. Finally, §§ 10 and 11 study the resolution of optical doublets in a uniform magnetic field.

A.—THE PHYSICAL INTERPRETATION OF TENSORS OF THE FORM $(T\psi, \phi)$.

§ 2. *Tensors in Hyperbolic Space-time.*

The assumed invariance of the wave equation (1.1) places severe restrictions upon the possible types of tensors with components of the form $(T\psi, \phi)$. The dominant consideration in enumerating all possible types is the hyperbolic character of space-time, *i.e.*, the distinctive character of the temporal co-ordinate.

In the first paper* of this series dealing with the operational wave equation, it was shown that to any transformation of the Lorentz group in (x_1, x_2, x_3, t) there corresponded one and only transformation of ψ which was of the form

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* 'Roy. Soc. Proc.,' A, vol. 127, p. 339 (1930).

$$\psi' = \mathrm{L}\psi,$$

and which left invariant both the wave equation and the expression (ψ, ψ).

In the analytical investigation it is convenient to use the imaginary co-ordinate $x_4 = \iota ct$. The ψ-transformation,

$$\psi' = \{1 + \tfrac{1}{2}e\mathrm{A}_m\mathrm{A}_n\}\,\psi,$$

then corresponds to the infinitesimal transformation,

$$x_m' = x_m + ex_n, \qquad x_n' = x_n - ex_m,$$

for all pairs of values of m and n. To obtain the real Lorentz transformations in (x_m, t) we must write $e = \iota\varepsilon$, where ε is real. The associated transformations are then

$$\left.\begin{aligned} x_m' &= x_m - \varepsilon ct, \\ ct' &= ct - \varepsilon x_m, \end{aligned}\right\} \quad \text{and} \quad \psi' = \{1 + \tfrac{1}{2}\varepsilon\iota\mathrm{A}_m\mathrm{A}_4\}\,\psi.$$

The ι concealed in x_4 was ignored in the paper cited above so that the results obtained there refer to elliptic space-time. Only a summary need be given of the corresponding results in hyperbolic space-time. They are as follows :—If ψ and ϕ are any two wave functions, all the invariants of the form $(\mathrm{T}\psi, \phi)$ are linear functions of

$$(\mathrm{A}_4\psi, \phi) \quad \text{and} \quad (\mathrm{A}_4\psi, \mathrm{E}\phi), \quad \text{where} \quad \mathrm{E} = \mathrm{A}_1\mathrm{A}_2\mathrm{A}_3\mathrm{A}_4\,; \tag{2.1}$$

all the 4-vectors with components of the same form are linear functions of the two fundamental 4-vectors J_μ and J_μ', where

$$\mathrm{J}_1 = +\,(\iota\mathrm{A}_4\mathrm{A}_1\psi, \phi), \quad \mathrm{J}_2 = +\,(\iota\mathrm{A}_4\mathrm{A}_2\psi, \phi), \quad \mathrm{J}_3 = +\,(\iota\mathrm{A}_4\mathrm{A}_3\psi, \phi),$$
$$\mathrm{J}_0 = (\psi, \phi), \tag{2.2}$$

and

$$\mathrm{J}_1' = (\iota\mathrm{A}_4\mathrm{A}_1\psi, \mathrm{E}\phi), \quad \mathrm{J}_2' = (\iota\mathrm{A}_4\mathrm{A}_2\psi, \mathrm{E}\phi), \quad \mathrm{J}_3' = (\iota\mathrm{A}_4\mathrm{A}_3\psi, \mathrm{E}\phi),$$
$$\mathrm{J}_0' = (\psi, \mathrm{E}\phi)\,; \tag{2.3}$$

and all the 6-vectors are linear functions of the fundamental 6-vector,

$$\left.\begin{aligned} \mathrm{M}_{23} &= (-\,\iota\mathrm{A}_2\mathrm{A}_3\psi, \mathrm{A}_4\phi), \ldots, \\ \mathrm{P}_{10} &= (\mathrm{A}_1\psi, \phi), \ldots, \end{aligned}\right\} \tag{2.4}$$

and its reciprocal.

§ 3. *The Charge and Current Tensor.*

The results of § 2 enable us to determine the charge and current tensor. We need the additional axiom that, if x is a real variable,

$$\frac{\partial}{\partial x}(\psi, \phi) = \left(\frac{\partial \psi}{\partial x}, \phi\right) + \left(\psi, \frac{\partial \phi}{\partial x}\right) \tag{3.1}$$

Since ι is a skew operator, it follows that

$$\mathbf{p}(\psi, \phi) = (\mathbf{p}\psi, \phi) - (\psi, \mathbf{p}\phi), \tag{3.2}$$

and

$$p_0(\psi, \phi) = (p_0\psi, \phi) - (\psi, p_0\phi). \tag{3.3}$$

If ψ and ϕ are any two wave-numbers,

$$2(\mathbf{p} \cdot \mathbf{J} - c^{-1}p_0 J_0) = +(\iota A_4 W\psi, \phi) + (\iota A_4\psi, W\phi),$$

and

$$2(\mathbf{p} \cdot \mathbf{J}' - c^{-1}p_0 J_0{}') = +(\iota E A_4 W\psi, \phi) - (\iota E A_4\psi, W\phi) + 2m_0 c\,(E A_4\psi, \phi).$$

Now the charge and current tensor must satisfy the equation of continuity,

$$\mathbf{p} \cdot \boldsymbol{\sigma} - c^{-1}p_0\rho = 0.$$

Hence, if ψ and ϕ are both wave-functions referring to two states of the atom, the charge and current tensor for the transition $\phi \rightarrow \psi$ must be a multiple of the 4-vector with components J_1, J_2, J_3, J_0. If the wave-functions ψ and ϕ refer to two quantised states, the wave-functions may be normalised so that, in the notation of (1.2),

$$[\psi, \psi] = 1 = [\phi, \phi].$$

The charge density is then

$$\rho = -eJ_0 = -e(\psi, \phi), \quad \text{(e.s.u.)}, \tag{3.4}$$

and the current density is

$$\boldsymbol{\sigma} = -e\mathbf{J} = -e(\iota A_4 \mathbf{A}\psi, \phi) \quad \text{(e.m.u.)} \tag{3.5}$$

Following Gordon* and Darwin† we may analyse the total charge and current densities into two parts which are usually attributed to convection and spin. Using the suffixes "c" and "s" to distinguish these parts, we find that

$$\rho = \rho_c + \rho_s, \qquad \boldsymbol{\sigma} = \boldsymbol{\sigma}_c + \boldsymbol{\sigma}_s,$$

where

$$\rho_c = \frac{e}{2m_0c^2}\{(A_4\psi, p_0\phi) + (p_0\psi, A_4\phi) + 2eV(A_4\psi, \phi)\}, \tag{3.6}$$

$$\boldsymbol{\sigma}_c = \frac{e}{2m_0c}\{(A_4\psi, \mathbf{p}\phi) + (\mathbf{p}\psi, A_4\phi) + 2ec^{-1}\mathbf{G}(A_4\psi, \phi)\}, \tag{3.7}$$

$$\rho_s = -\frac{eh}{4\pi m_0 c}\,\mathrm{div}\,\mathbf{P}, \tag{3.8}$$

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* 'Z. Physik,' vol. 50, p. 630 (1928).

† 'Roy. Soc. Proc.,' A, vol. 120, p. 621 (1928).

and

$$\boldsymbol{\sigma}_s = \frac{eh}{4\pi m_0 c}\left\{\text{curl}\,\mathbf{I} + \frac{\partial \mathbf{P}}{c\,\partial t}\right\}. \tag{3.9}$$

I and **P** are the constituents of the fundamental 6-vector found in § 2 ;

$$\mathbf{I} = \tfrac{1}{2}(-\iota \mathbf{A}_{\wedge} \mathbf{A}\psi,\ \mathrm{A}_4\phi), \tag{3.91}$$

and

$$\mathbf{P} = (\mathbf{A}\psi,\ \phi). \tag{3.92}$$

I is the magnetisation and **P** the polarisation, due to the spin, the unit being one magneton, $(eh/4\pi m_0 c)$, per unit volume.

B.—THE GENERAL PROPERTIES OF MATRIX ELEMENTS.

§ 4. *Pseudo-Hermitian Operators.*

The fundamental principle which underlies the methods of determining the integrated tensors of the form $[\mathrm{T}\psi,\ \phi]$ is a corollary to the axiom introduced in § 3. It follows from (3.2) that

$$[\mathbf{p}\psi,\ \phi] - [\psi,\ \mathbf{p}\phi] = \int \mathbf{p}\,(\psi,\ \phi)\,dx_1\,dx_2\,dx_3.$$

If ψ or ϕ refers to a quantised state, the volume integral may be transformed into a surface integral which tends to zero as the surface recedes to infinity. Hence

$$[\mathbf{p}\psi,\ \phi] = [\psi,\ \mathbf{p}\phi]. \tag{4.1}$$

Operators which satisfy the same condition as **p** will be called pseudo-Hermitian to distinguish them from Hermitian operators which satisfy the more stringent condition that

$$(\mathbf{p}\psi,\ \phi) = (\psi,\ \mathbf{p}\phi).$$

The pseudo-Hermitian character of **p** simplifies the expression for the magnetic moment. If the atom is in the quantised state determined by ψ, the magnetic moment due to the convection current $\boldsymbol{\sigma}_c$ is

$$\tfrac{1}{2}\int \mathbf{x}_{\wedge}\,\boldsymbol{\sigma}_c\,dx_1\,dx_2\,dx_3 = \frac{e}{2m_0 c}[\mathbf{m}\psi,\ \mathrm{A}_4\psi], \tag{4.2}$$

in the absence of an external magnetic field ($\mathbf{G} = 0$), **m** being the orbital momentum operator $\mathbf{x}_{\wedge}\mathbf{p}$. Also, since

$$p_0(\psi,\ \psi) = (p_0\psi,\ \psi) - (\psi,\ p_0\psi) = 0,$$

therefore

$$\partial \mathrm{P}/\partial t = 0\,;$$

and the magnetic moment due to the spin current $\boldsymbol{\sigma}_s$ is

$$\tfrac{1}{2}\int \mathbf{x}\wedge\boldsymbol{\sigma}_s\,dx_1\,dx_2\,dx_3 = \frac{eh}{4\pi m_0 c}\int \mathbf{I}\,dx_1\,dx_2\,dx_3.$$

On integrating by parts, and this expression equals

$$\frac{eh}{4\pi m_0 c}[\mathbf{S}\psi,\ A_4\psi], \tag{4.3}$$

where $\mathbf{S}$ is the spin operator $-\tfrac{1}{2}\iota\mathbf{A}\wedge\mathbf{A}$.

§ 5. *Matrix Elements and Selection Rules.*

A hydrogen-like atom free from the action of external fields possesses the four reducible operators

$$\left.\begin{aligned} M_3 &= m_3 + \tfrac{1}{2}\mathfrak{h}S_3, \\ Q &= A_4(\mathbf{m}\,.\,\mathbf{S} + \mathfrak{h}), \\ H &= \iota c A_4 W + p_0 \\ &= \iota c A_4 \mathbf{A}\,.\,\mathbf{p} - eV - \varepsilon_0 A_4, \\ \text{and}\quad F &= \iota c W + \varepsilon_0, \end{aligned}\right\} \tag{5.1}$$

where $\varepsilon_0 = m_0 c^2$.

The first three of these operators are pseudo-Hermitian. Hence we adopt the following notation for matrix elements.

Let ω_a be a wave-number, independent of t, and therefore not a wave-function, satisfying the equations,

$$\left.\begin{aligned} M_3\omega_a &= u_a\mathfrak{h}\omega_a,^* \\ Q\omega_a &= \mu_a\mathfrak{h}\omega_a, \\ H\omega_a &= \varepsilon_a\omega_a, \\ \text{and}\quad [\omega_a,\ \omega_a] &= 1, \quad \text{if } \varepsilon_a < \varepsilon_0. \end{aligned}\right\} \tag{5.2}$$

Then the " a, b-matrix element " of any operator R, referring to a transition from the state a to the state b, is defined as

$$R(a, b) \equiv R(\varepsilon_a,\ \mu_a,\ u_a\,;\ \ \varepsilon_b,\ \mu_b,\ u_b) = [R\omega_b,\ \omega_a]. \tag{5.3}$$

If either or both of the energy levels, ε_a and ε_b, belong to the continuous range (*i.e.*, ε_a, $\varepsilon_b > \varepsilon_0$), the corresponding matrix elements vary with the system of ω-functions employed. This ambiguity may be removed by normalising the

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[*] $\mathfrak{h} = h/(2\pi)$, where $\mathfrak{h}$ is Planck's constant.

ω-functions in the continuous range of energy levels as well as in the discrete range; but, as transitions in the discrete range only are considered in this paper, it is unnecessary to carry out the process of normalisation.

The calculation of the matrix elements of any operator R depends only upon the relations connecting R with the three reducible, pseudo-Hermitian operators, M_3, Q and H. The simplest type of relation is of the form,

$$g(\Gamma, \mathrm{R}) = 0, \tag{5.4}$$

where g is a polynomial in Γ and R, and Γ is one of the operators, M_3, Q or H. From this type of relation we can deduce at once which matrix elements of R are necessarily zero.

For, by operating on a wave-number ω_b with the operator $g(\Gamma, \mathrm{R})$, we obtain a relation of the form

$$\left.\begin{aligned} f(\Gamma, \gamma_b)\,\mathrm{R}\omega_b &= 0, \\ \text{where} \qquad \Gamma\omega_b &= \gamma_b\omega_b, \end{aligned}\right\} \tag{5.5}$$

and f is a polynomial in Γ and γ_b. Since f is necessarily a reducible, pseudo-Hermitian operator, it follows that

$$f(\gamma_a, \gamma_b)\,.\,\mathrm{R}(a, b) = [\mathrm{R}\omega_b, f(\gamma_a, \gamma_b)\,\omega_a]$$

$$= [\mathrm{R}\omega_b, f(\Gamma, \gamma_b)\,\omega_a] = [f(\Gamma, \gamma_b)\,\mathrm{R}\omega_b, \omega_a] = 0.$$

Hence

$$\mathrm{R}(a, b) = 0 \quad \text{unless} \quad f(\gamma_a, \gamma_b) = 0. \tag{5.6}$$

This is the "selection rule" for the operator R and the quantum number γ.

For example, since A_4 commutes with M_3 and Q

$$g(\Gamma, A_4) \equiv \Gamma A_4 - A_4\Gamma = 0,$$

where Γ stands for M_3 or Q. Hence

$$f(\Gamma, \gamma_b)\,A_4\omega_b = g(\Gamma, A_4)\,\omega_b = (\Gamma - \gamma_b)\,A_4\omega_b = 0,$$

whence

$$\left.\begin{aligned} A_4(a, b) = 0 \ \text{ unless } \ u_a &= u_b, \\ \text{and } \ \mu_a &= \mu_b. \end{aligned}\right\} \tag{5.7}$$

Again, since unity commutes with M_3, Q and H, it follows that

$$\left.\begin{aligned} 1(a, b) \equiv [\omega_b, \omega_a] = 0 \quad \text{unless} \quad u_a &= u_b, \\ \mu_a &= \mu_b, \\ \text{and} \quad \varepsilon_a &= \varepsilon_b. \end{aligned}\right\} \tag{5.8}$$

Hence, the ω-functions form an infinite set of orthogonal functions.

§ 6. *The Standard Approximations to the Wave Functions.*

The calculation of the matrix elements is facilitated by the use of the standard approximation to the ω-functions introduced by Dirac and Darwin. We divide ω into two parts, ξ and η, such that

and

$$\left.\begin{aligned} \xi &= \tfrac{1}{2}(1 - \mathrm{A}_4)\,\omega, & \eta &= \tfrac{1}{2}(1 + \mathrm{A}_4)\,\omega, \\ \omega &= \xi + \eta, & \mathrm{A}_4\omega &= -\,\xi + \eta. \end{aligned}\right\} \tag{6.1}$$

Then, on expanding the equations,

$$\tfrac{1}{2}(1 \pm \mathrm{A}_4)(\mathrm{H} - \varepsilon)\,\omega = 0,$$

we find that

and

$$\left.\begin{aligned} (\varepsilon_0 - \varepsilon - e\mathrm{V})\,\xi &= \iota c\mathbf{A}\,.\,\mathbf{p}\eta, \\ (\varepsilon_0 + \varepsilon + e\mathrm{V})\,\eta &= \iota c\mathbf{A}\,.\,\mathbf{p}\xi. \end{aligned}\right\} \tag{6.2}$$

Now, in a quantised state,

$$(1 - \alpha^2 \mathrm{Z}^2)^{\frac{1}{2}} \leqslant \varepsilon/\varepsilon_0 < 1,$$

where α is the fine structure constant and Z the effective nuclear number. Hence, to a first approximation, $\varepsilon_0 - \varepsilon$ may be neglected in comparison with ε_0, and η in comparison with ξ. The standard approximation to ω is, therefore,

$$\omega \sim \xi, \qquad (\varepsilon < \varepsilon_0). \tag{6.3}$$

It is now possible to obtain approximate values for the matrix elements of A_4 and of the eight operators which anti-commute with it, namely, E and $\mathrm{A}_4\mathrm{E}$, and the components of **A** and $\mathrm{A}_4\mathbf{A}$. These approximate values are useful in comparing the present theory with the theory of the spinning electron.

A_4 :—

From equations (6.1) and (6.3) it follows that $\mathrm{A}_4\omega \sim -\,\omega$, whence

$$\left.\begin{aligned} \mathrm{A}_4(a, b) &\sim 0 \quad \text{if} \quad a \neq b, \\ &\sim -1 \quad \text{if} \quad a = b. \end{aligned}\right\} \tag{6.4}$$

Since ψ_a and ω_a differ only in an exponential time factor, $\mathrm{A}_4\psi_a \sim -\,\psi_a$ also. Hence the magnetic moments due to convection and spin are respectively

$$-\frac{e}{2m_0c}[\mathbf{m}\psi,\,\psi] \quad \text{and} \quad -\frac{e}{m_0c}[\tfrac{1}{2}\mathfrak{h}\mathbf{S}\psi,\,\psi], \tag{6.41}$$

by equations (4.2) and (4.3), to the standard degree of approximation. But the total mechanical momenta due to convection and spin are respectively

$$[\mathbf{m}\psi,\ \psi] \quad \text{and} \quad [\tfrac{1}{2}\mathfrak{h}\mathbf{S}\psi,\ \psi]. \tag{6.42}$$

Hence the ratios of the magnetic to the mechanical momenta due to convection and spin are in agreement with the values assumed by Uhlenbeck and Goudsmit for the spinning electron.

A and A_4**A** :—

To obtain the matrix elements of $A_4\mathbf{A}$ we note that

$$[A_4\mathbf{A}\omega_b,\ \omega_a] = -[\mathbf{A}\xi_b,\ \xi_a] - [\mathbf{A}\eta_b,\ \xi_a] + [\mathbf{A}\xi_b,\ \eta_a] + [\mathbf{A}\eta_b,\ \eta_a],$$

while

$$[\mathbf{A}A_4\omega_b,\ \omega_a] = -[\mathbf{A}\xi_b,\ \xi_a] + [\mathbf{A}\eta_b,\ \xi_a] - [\mathbf{A}\xi_b,\ \eta_a] + [\mathbf{A}\eta_b,\ \eta_a].$$

Since A_4 anti-commutes with **A**, it follows that

$$[A_4\mathbf{A}\omega_b,\ \omega_a] = [\mathbf{A}\xi_b,\ \eta_a] - [\mathbf{A}\eta_b,\ \xi_a]$$

and

$$-[\mathbf{A}\xi_b,\ \xi_a] + [\mathbf{A}\eta_b,\ \eta_a] = 0.$$

But, by (6.2)

$$(\varepsilon_0 + \varepsilon + eV)\,\mathbf{A}\eta = c\,(\iota\mathbf{p} + \mathbf{S}_{\wedge}\,\mathbf{p})\,\xi,$$

whence

$$\mathbf{A}\eta \sim \frac{1}{2m_0c}(\iota\mathbf{p} + \mathbf{S}_{\wedge}\,\mathbf{p})\,\xi.$$

Therefore

$$[A_4\mathbf{A}\omega_b,\ \omega_a] \sim -\frac{\iota}{m_0c}[\mathbf{p}\xi_b,\ \xi_a], \tag{6.5}$$

also

$$\mathbf{A} = \tfrac{1}{2}\iota A_4\mathbf{A}_{\wedge}\,A_4\mathbf{S}. \tag{6.6}$$

The significance of the first relation (6.5) is seen more clearly on introducing the wave-operator

$$\boldsymbol{\alpha} = \iota A_4\mathbf{A}, \tag{6.51}$$

and the velocity operator

$$\mathbf{v} = \frac{1}{m_0}\mathbf{p}. \tag{6.52}$$

Then

$$\boldsymbol{\alpha}\,(a,\ b) \sim \frac{1}{c}\,\mathbf{v}\,(a,\ b), \tag{6.53}$$

while the wave-equation, $(\mathrm{H} - \varepsilon)\,\omega = 0$, becomes

$$\left.\begin{aligned}(\boldsymbol{\alpha} \,.\, \mathbf{p} - e\mathrm{V})\,\omega &= (\mathrm{A}_4\varepsilon_0 + \varepsilon)\,\omega \\ &\sim (\varepsilon - \varepsilon_0)\,\omega\end{aligned}\right\} \qquad (6.54)$$

These results indicate in what sense we may associate the operators $\boldsymbol{\alpha}$ and $\mathbf{v}$ as suggested by Fock* and Briet.†

To interpret the second relation (6.6), we recall that the total electric moment due to spin is the integral of $\mathbf{x}\rho_s$, which by equations (3.8) and (3.92) equals

$$\frac{e}{2m_0c}\,\mathfrak{h}\,[\mathbf{A}\psi_b,\ \psi_a]\,; \qquad (6.61)$$

while the total magnetic moment due to spin is, by (4.3),

$$\frac{e}{2m_0c}\,\mathfrak{h}\,[\mathbf{S}\psi_b,\ \mathrm{A}_4\psi_a]. \qquad (6.62)$$

Hence the relation (6.6) replaces Frenkel's kinematic relation‡ and expresses the spin electric moment as $\frac{1}{2c}$ times the vector product of the electronic velocity (here represented by $\mathbf{v}$) and the spin magnetic moment.

The spin energy of the atom, *i.e.*, the energy of its spin electric moment and spin magnetic moment, is easily seen to be

$$-\frac{e}{2m_0c}\,\mathfrak{h}\,[\,(\mathbf{E}\,.\,\mathbf{A} + \mathbf{H}\,.\,\mathrm{A}_4\mathbf{S})\,\psi_b,\ \psi_a] \qquad (6.63)$$

from the expressions (6.61) and (6.62), **E** and **H** being the electric and magnetic intensities at any point. By using the relation (6.6) this expression reduces to

$$\frac{e}{2m_0c}\,\mathfrak{h}\,[\mathbf{H}'\,.\,\mathbf{S}\,\psi_b,\ \psi_a], \qquad (6.64)$$

where

$$\mathbf{H}' = \mathbf{H} + \frac{1}{2c}\,\mathbf{E}_{\wedge}\mathbf{v}. \qquad (6.65)$$

This is in agreement with Thomas' theory of the spinning electron.

E and $\mathbf{A}_4\mathbf{E}$:—

Finally, we note that

$$\mathrm{HE} - \mathrm{EH} = 2\mathrm{EA}_4\varepsilon_0,$$

whence

$$\mathrm{E}\,(a, b) \sim 0 \quad \text{and} \quad (\mathrm{A}_4\mathrm{E})\,(a, b) \sim 0. \qquad (6.7)$$

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* 'Z. Physik,' vol. 55, p. 127 (1929).

† 'Proc. Nat. Acad. Sci.,' vol. 14, p. 553 (1928).

‡ 'Z. Physik,' vol. 37, p. 248 (1926).

§ 7. *The Matrix Law of Multiplication.*

The first order wave-equation may be written in the form

where

$$\left.\begin{aligned}&(\mathrm{F}-\varepsilon_0)\,\omega=0,\\ &\mathrm{F}=\iota c\mathbf{p}\,.\,\mathbf{A}-(\varepsilon+e\mathrm{V})\,\mathrm{A}_4,\quad(5.1),\end{aligned}\right\}\tag{7.1}$$

and is an operator which anti-commutes with E. The selection rule for unity regarded as an operator (5.8), shows that the ω-functions derived from this first order equation form an infinite set of orthogonal functions. But this set of functions is not "complete," as was first pointed out by Darwin. Under these circumstances the most natural procedure is to consider the second order wave-equation

$$(\mathrm{F}+\varepsilon_0)(\mathrm{F}-\varepsilon_0)\,\omega=(\mathrm{F}^2-\varepsilon_0{}^2)\,\omega=0,\tag{7.2}$$

and the totality of its solutions. Since

$$(\mathrm{F}+\varepsilon_0)\,\mathrm{E}\omega=-\mathrm{E}\,(\mathrm{F}-\varepsilon_0)\,\omega,$$

to any solution, ω, of the first order equation (7.1) there corresponds a pair of solutions, ω and Eω, of the second order equation (7.2). We shall assume that the infinite set of functions, ω_a and $\mathrm{E}\omega_a$, although not an orthogonal set, is "closed" in the sense that, if a wave-number χ satisfies the equations,

$$\left.\begin{aligned}&[\chi,\,\omega_a]=0=[\chi,\,\mathrm{E}\omega_a],\\ &\text{for all functions of the set, then }\chi\equiv0.\end{aligned}\right\}\tag{7.3}$$

Since the set of ω-functions is not closed, the matrix law of multiplication used by Dirac is, in general, false. Nevertheless we shall show that it is true, to the standard degree of approximation, for all the operators required in the theory of the Zeeman effect, namely, for **M**, **S** and **x**. This justifies Dirac's method of obtaining matrix elements.

The essence of the proof consists in showing that $[\mathrm{R}\omega_b,\,\mathrm{E}\omega_a]$ is approximately zero for all pairs of ω-functions such that $\varepsilon_b<\varepsilon_0$, provided that R commutes with A_4. It is known from the selection rules for R that the number of non-vanishing matrix elements, $\mathrm{R}\,(a,\,b)=[\mathrm{R}\omega_b,\,\omega_a]$, is finite. Hence, if

$$\chi=\mathrm{R}\omega_b-\sum_a\omega_a\mathrm{R}\,(a,\,b),$$

$$[\chi,\,\omega_a]=0,$$

and

$$[\chi,\,\mathrm{E}\omega_a]=\text{a finite number of small quantities,}$$

in virtue of the results of (6.7) and the lemma concerning $[\mathrm{R}\omega_b, \mathrm{E}\omega_a]$. Therefore, by (7.3),

$$\mathrm{R}\omega_b \sim \sum_a \omega_a \mathrm{R}(a, b). \tag{7.4}$$

If S is an operator of the same character as R,

$$\mathrm{S}\omega_a \sim \sum_a \omega_c \mathrm{S}(c, a).$$

Hence

$$(\mathrm{SR})\,\omega_b \sim \sum_{c,\,a} \omega_c \mathrm{S}(c, a)\,\mathrm{R}(a, b),$$

and

$$(\mathrm{SR})(c, b) \sim \sum_a \mathrm{S}(c, a)\,\mathrm{R}(a, b), \tag{7.5}$$

—the usual form of the matrix law of multiplication.

To prove the lemma we write R in the form $\mathrm{X}f(x_1, x_2, x_3)$ where X is any one of the eight operators ($\mathrm{A}_1\mathrm{E}$, $\mathrm{A}_2\mathrm{E}$, $\mathrm{A}_3\mathrm{E}$, 1 ; S_1, S_2, S_3, A_4), which commute with A_4. Then

$$\mathrm{A}_4(\mathrm{HXE}f - \mathrm{XE}f\mathrm{H}) - (\mathrm{HXE}f - \mathrm{XE}f\mathrm{H})\,\mathrm{A}_4 = -4\varepsilon_0\mathrm{XE}f.$$

Hence

$$(\mathrm{ER})(a, b) = (\mathrm{EX}f)(a, b) = \pm(\mathrm{XE}f)(a, b) \sim 0. \tag{7.6}$$

The eight operators which anti-commute with A_4 do not obey the matrix law of multiplication.

To ensure that the matrix elements of a pseudo-Hermitian operator R shall form a Hermitian matrix, so that

$$\mathrm{R}(a, b) = \mathrm{R}^*(b, a), \tag{7.7}$$

we introduce the additional axiom that (ψ, ϕ) and (ϕ, ψ) are conjugate complex numbers.

C.—SPECIAL MATRIX ELEMENTS.

§ 8. *The Standard Quantum Numbers.*

The distinctive feature of the operational wave-equation is the emergence of the reducible operator $\mathrm{Q} = \mathrm{A}_4(\mathbf{m} \, . \, \mathbf{S} + \mathfrak{h})$. Since Q depends upon the scalar product of the mechanical momenta due to convection and spin, it may be called "the interaction operator," and the associated quantum number μ the "interaction quantum number." In the previous paper* μ was wrongly identified and its possible values were incorrectly enumerated. The correct investigation into the nature of μ is as follows.

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* 'Roy. Soc. Proc.,' A, vol. 127, p. 359 (1930). The error is due to the fact that $(\mathrm{G}-g)\phi$ is a good approximation to ϕ only when μ is negative (see equation (7.5)).

When the radial quantum number, n', differs from zero, the energy levels are given by equation (5.9) of the previous paper as

$$\frac{\varepsilon}{\varepsilon_0} = \left\{1 - \frac{\alpha^2 Z^2}{[n' + (\mu^2 - \alpha^2 Z^2)^{\frac{1}{2}}]^2}\right\}^{-\frac{1}{2}}. \tag{8.1}$$

But, when $n' = 0$, the expression for ξ reduces to a single term, $\xi_0 x^{g-1}$, and ζ_0 satisfies the equations

$$G\xi_0 = -g\xi_0 \quad \text{and} \quad F\xi_0 = \lambda\xi_0, \tag{8.11}$$

where

$$F = -(EA_4\varepsilon + E\varepsilon_0)/(\mathfrak{h}c),$$

$$G = -(\mu A_4 + EA_4 Z\alpha),$$

$$\lambda = (\varepsilon_0{}^2 - \varepsilon^2)^{\frac{1}{2}}/(\mathfrak{h}c),$$

and

$$g = (\mu^2 - \alpha^2 Z^2)^{\frac{1}{2}}.$$

We rewrite equations (8.11) as

$$\left.\begin{aligned} A_4\mu\xi_0 + EA_4\alpha Z\xi_0 &= g\xi_0, \\ A_4\varepsilon_0\xi_0 - EA_4\lambda\mathfrak{h}c\xi_0 &= -\varepsilon\xi_0, \end{aligned}\right\} \tag{8.12}$$

having multiplied the second equation by $EA_4 \,.\, \mathfrak{h}c$.
It follows from equations (8.12) that

$$\frac{\mu}{\varepsilon_0} = -\frac{\alpha Z}{\lambda\mathfrak{h}c} = -\frac{g}{\varepsilon}, \tag{8.13}$$

where μ is negative and $\varepsilon/\varepsilon_0 = |g/\mu|$. This expression for the energy level agrees with (8.1) when $n' = 0$. If the principal quantum number, n, is defined as

$$n = n' + |\mu|, \tag{8.14}$$

it is clear that the possible values of μ for a fixed value of n are

$$\mu = \pm 1, \pm 2, \ldots \pm (n-1), -n. \tag{8.15}$$

The interaction quantum number, here called μ, is written j by Dirac and $-k$ by Sommerfeld.

For classificatory purposes μ is replaced by the serial quantum number l and the inner quantum number j, which are defined in terms of the diagonal matrix elements of $\mathbf{m}^2$ and $\mathbf{M}^2$ respectively. We write

$$\left.\begin{aligned} &\mathbf{M}^2(a, a) = j_a(j_a + 1)\mathfrak{h}^2, \quad j_a > 0, \\ \text{and} \quad &\mathbf{m}^2(a, a) \sim l_a(l_a + 1)\mathfrak{h}^2, \quad l_a > 0. \end{aligned}\right\} \tag{8.2}$$

It follows from the relations

$$M^2 = Q^2 - \tfrac{1}{4}\mathfrak{h}^2,$$

$$m^2 = Q^2 - \mathfrak{h} A_4 Q \sim Q^2 + \mathfrak{h} Q,$$

and the integral character of l, that

and

$$\left.\begin{array}{l} j_a = |\mu_a| - \tfrac{1}{2}, \\ l_a = |\mu_a + \tfrac{1}{2}| - \tfrac{1}{2} \end{array}\right\}. \qquad (8.21)$$

The possible values of l are 0, 1, 2, ... $(n - 1)$ (8.22)

The possible values of the equatorial quantum number u (usually denoted by m) range in integral steps from $-j$ to $+j$ and hence are $2j + 1$ in number. In the absence of an external field the energy levels defined by fixed values of n and l have different inner quantum numbers, $j = l \pm \frac{1}{2}$, and they are assigned different statistical weights, $2j + 1 = 2(l + 1)$ or $2l$. From (8.1) the energy levels are given by

$$\varepsilon - \varepsilon_0 \sim -\frac{RhZ^2}{n^2} - \frac{Rh\alpha^2 Z^4}{n^3}\left\{\frac{1}{j + \frac{1}{2}} - \frac{3}{4n}\right\}, \qquad (8.3)$$

where R, the Rydberg constant $= 2\pi^2 m_0 e^4 h^{-3}$. Hence the "optical centre of gravity" of the doublet, calculated from the statistical weights of the energy levels, is at ε_c, where

$$\varepsilon_c - \varepsilon_0 \sim -\frac{RhZ^2}{n^2} - \frac{Rh\alpha^2 Z^4}{n^3}\left\{\frac{1}{l + \frac{1}{2}} - \frac{3}{4n}\right\}; \qquad (8.31)$$

and the doublet separation is

$$\delta = |\varepsilon_1 - \varepsilon_2| \sim \frac{Rh\alpha^2 Z^4}{n^3} \cdot \frac{1}{l(l + 1)}. \qquad (8.32)$$

Hence

or

$$\left.\begin{array}{ll} \varepsilon - \varepsilon_c \sim l\,\dfrac{\frac{1}{2}\delta}{l + \frac{1}{2}} & \text{if} \quad j = l + \tfrac{1}{2}, \\ -(l + 1)\,\dfrac{\frac{1}{2}\delta}{l + \frac{1}{2}} & \text{if} \quad j = l - \tfrac{1}{2} \end{array}\right\}. \qquad (8.33)$$

The standard formulæ are

$$\varepsilon - \varepsilon_c = \left\{(j - l) - \frac{\frac{1}{4}}{l + \frac{1}{2}}\right\}\delta = \gamma_w \delta, \qquad (8.34)$$

where

$$\gamma_w = \frac{j(j + 1) - l(l + 1) - \frac{3}{4}}{2(l + \frac{1}{2})}, \qquad (8.35)$$

—Landé's γ-factor for weak fields.

§ 9. *The Momentum and Polarisation Matrices.*

By the theorem of § 7 the matrix law of multiplication may be used in calculating the matrix elements of **M**, **S** and **x**. Since the operators **M** and **x** are connected by the same relations as in the theory of the spinning electron, the present theory simply reproduces the same values for the matrix elements. The deduction of the selection rule for **x** is, however, somewhat shortened.

Starting from the relation

$$\mathbf{F}_1 \equiv \mathrm{Q}\mathbf{x} - \mathbf{x}\mathrm{Q} = \hbar \mathbf{x}_{\wedge} \mathrm{AE}, \tag{9.1}$$

we deduce that

$$\mathbf{F}_2 \equiv \mathrm{Q}\mathbf{F}_1 - \mathbf{F}_1\mathrm{Q} = \hbar^2\mathbf{x} + 2\hbar\,(\mathbf{x}\,.\,\mathbf{S})\,\mathbf{M},$$

and

$$\mathbf{F}_3 \equiv \mathrm{Q}\mathbf{F}_2 + \mathbf{F}_2\mathrm{Q} = \hbar^2\,(\mathrm{Q}\mathbf{x} + \mathbf{x}\mathrm{Q}).$$

On expanding $\mathbf{F}_3$ we obtain the relations

$$g\,(\mathrm{Q},\,\mathbf{x}) \equiv \mathrm{Q}^3\mathbf{x} - \mathrm{Q}^2\mathbf{x}\mathrm{Q} - \mathrm{Q}\mathbf{x}\mathrm{Q}^2 + \mathbf{x}\mathrm{Q}^3 - \hbar^2\,(\mathrm{Q}\mathbf{x} + \mathbf{x}\mathrm{Q}) = 0,$$

(compare equation (5.4)), and

$$f\,(\mathrm{Q},\,\mu_b\hbar)\,\mathbf{x}\omega_b = 0,$$

where

$$f\,(a,\,b) = (a + b)\,(a - b - 1)\,(a - b + 1).$$

Hence

$$\mathbf{x}\,(a,\,b) = 0$$

unless

$$\mu_a = -\,\mu_b, \quad \mu_b + 1, \quad \text{or} \quad \mu_b - 1. \tag{9.11}$$

In terms of the standard quantum numbers this selection rule is

$$\Delta l = \pm\,1, \quad \Delta j = 0 \quad \text{or} \quad \pm\,1. \tag{9.12}$$

The selection rule for the equatorial quantum number u is the same as in the earlier theory, *i.e.*,

$$\Delta u = 0 \quad \text{or} \quad \pm\,1. \tag{9.13}$$

The only spin operator for which matrix elements are required is S_3. The fundamental relations involving S_3 are

$$\mathrm{M}_3\mathrm{S}_3 - \mathrm{S}_3\mathrm{M}_3 = 0, \tag{9.21}$$

$$\mathrm{F}_1 \equiv \mathrm{QS}_3 + \mathrm{S}_3\mathrm{Q} = 2\mathrm{A}_4\mathrm{M}_3 + \hbar\mathrm{A}_4\mathrm{S}_3, \tag{9.22}$$

and

$$\mathrm{S}_3\mathrm{H} - \mathrm{H}_3\mathrm{S} = 2c\mathrm{A}_4\,(\mathrm{A}_1p_2 - \mathrm{A}_2p_1). \tag{9.23}$$

From (9.21) it follows that

$$\mathrm{S}_3\,(a,\,b) = 0 \quad \text{unless} \quad u_a = u_b. \tag{9.24}$$

From (9.22) it follows that

$$F_2 \equiv QF_1 + F_1Q = 4A_4M_3Q + 2\mathfrak{h}M_3 + \mathfrak{h}^2S_3,$$

and

$$F_3 \equiv QF_2 - F_2Q = \mathfrak{h}^2(QS_3 - S_3Q).$$

Now

$$F_3 \equiv Q^3S_3 + Q^2S_3Q - QS_3Q^2 - SQ^3.$$

Hence

$$f(Q,\ \mu_b\mathfrak{h})\ S_3\omega_b = 0,$$

where

$$f(a, b) = (a - b)(a + b - 1)(a + b + 1).$$

Therefore

$$S_3(a, b) = 0 \quad \text{unless} \quad \mu_a = \mu_b, \quad -\mu_b + 1 \quad \text{or} \quad -\mu_b - 1. \tag{9.25}$$

From (9.23) it follows that

$$A_4(S_3H - H_3S) + (S_3H - HS_3)A_4 = 0.$$

Hence to the standard degree of approximation

$$(\varepsilon_a - \varepsilon_b) \,.\, S_3(a, b) \sim 0,$$

i.e.,

$$S_3(a, b) = 0 \quad \text{unless} \quad \varepsilon_a \sim \varepsilon_b. \tag{9.26}$$

The last condition implies that the states "*a*" and "*b*" have the same total quantum number *n*. Hence in writing the matrix elements of S_3 we can omit reference to *n* and write

$$S_3(a, b) = S_3(\mu_a, u_a\,;\ \mu_b, u_b).$$

Using the standard approximation we deduce from (9.22) that

$$S_3(\mu, u\,;\ \mu, u) \sim \frac{-u}{\mu + \frac{1}{2}}, \tag{9.31}$$

and

$$S_3(\mu, u\,;\ -\mu + 1, u) \sim 0. \tag{9.32}$$

Also, since $S_3{}^2 = 1$, it follows that

$$|S_3(\mu, u\,;\ \mu, u)|^2 + |S_3(\mu, u\,;\ -\mu - 1, u)|^2 = 1,$$

whence

$$|S_3(\mu, u\,;\ -\mu - 1, u)|^2 = 1 - \frac{u^2}{(\mu + \frac{1}{2})^2}. \tag{9.33}$$

D.—THE ZEEMAN EFFECT.

§ 10. *The Resolution of an Optical Doublet.*

The Zeeman effect is most easily discussed on the basis of the second order wave-equation (7.2)

where

$$\left.\begin{aligned} (F^2 - \varepsilon_0^2)\,\omega &= 0, \\ F &= \iota c\,(\mathbf{p} + ec^{-1}\mathbf{G})\,\mathbf{A} - (\varepsilon + eV)\,A_4, \end{aligned}\right\} \qquad (10.1)$$

the external magnetic field being allowed for by the introduction of the term in **G**. For a uniform field of strength **H**,

$$\mathbf{G} = \tfrac{1}{2}\mathbf{H}_{\wedge}\mathbf{x}.$$

The explicit form of the second order wave-equation is

$$\{c^2(\mathbf{p} + ec^{-1}\mathbf{G})^2 - (\varepsilon + eV)^2 + \varepsilon_0^2 + ec\mathfrak{h}\,(\mathbf{H}\,.\,\mathbf{S} + A_4\mathbf{E}\,.\,\mathbf{A})\}\,\omega = 0. \qquad (10.11)$$

It is convenient to write

$$\varepsilon = \varepsilon_0 + U,$$

and to group together the various terms of (10.11) as follows :—

$$\left.\begin{aligned} H_0 &= \frac{1}{2m_0}\,\mathbf{p}^2 - eV, \\ H_R &= -\frac{1}{2m_0c^2}\,\{U^2 + 2U\,.\,eV + e^2V^2\}, \\ H_M &= \frac{e}{2m_0c}\,\mathbf{m}\,.\,\mathbf{H}, \\ H_S &= \frac{e\mathfrak{h}}{2m_0c}\,(\mathbf{H}\,.\,\mathbf{S} + A_4\mathbf{E}\,.\,\mathbf{A}), \end{aligned}\right\} \qquad (10.12)$$

so that the equation becomes

$$(H_0 + H_R + H_M + H_S - U)\,\omega = 0, \qquad (10.13)$$

neglecting $\mathbf{G}^2$. It appears from (6.63) that H_S is the spin energy operator, since $A_4 \sim -1$ to the standard degree of approximation.

To exhibit the influence of the magnetic field in modifying the relativistic fine structure of the term series we put equation (10.13) in the form

where

and

$$\left.\begin{aligned} (D - \varepsilon)\,\omega + oZ\omega &= 0, \\ D &= H_0 + H_R + \frac{e\mathfrak{h}}{2m_0c}\,A_4\mathbf{E}\,.\,\mathbf{A} + \varepsilon_0, \\ Z &= \tfrac{1}{2}S_3 + \mathfrak{h}^{-1}M_3, \\ o &= \frac{e\mathfrak{h}}{2m_0c}\,.\,H_3, \end{aligned}\right\} \qquad (10.2)$$

taking the *z*-axis in the direction of the magnetic field.

It follows from equations (9.31), (9.32), and (9.33) that, in general, the surviving matrix elements of the Zeeman operator Z refer to transitions of the type, $u \rightarrow u$, $\mu \rightarrow \mu$ or $-\mu - 1$, $n \rightarrow n$, in which n, l, u are fixed while j changes from $l + \frac{1}{2}$ to $l - \frac{1}{2}$. But, if u has its lowest value (for a chosen value of l) namely, $-(l + \frac{1}{2})$, then μ is negative and j has only one possible value, namely $(l + \frac{1}{2})$. In this case only the diagonal elements of the Z-matrix survive. We treat these two possibilities separately.

$u = -(l + \frac{1}{2})$.

Let ω be an ω-function for the undisturbed atom with quantum numbers n, l, u, $= -l - \frac{1}{2}$ and energy ε_c. Then

and
$$\left.\begin{aligned} D\omega &= \varepsilon_c \omega, \\ Z\omega &= -(l+1)\,\omega. \end{aligned}\right\} \tag{10.31}$$

Hence the change of energy due to the magnetic field is

$$\varepsilon - \varepsilon_c = -(l+1)\,o, \tag{10.32}$$

by the first of equations (10.2).

$u > -(l + \frac{1}{2})$.

Let ω_1 and ω_2 be ω-functions for the undisturbed atom with quantum numbers n, l, u and $j = l \pm \frac{1}{2}$ respectively, and energies ε_1 and ε_2. Then the solutions of (10.2) are of the form

$$\Omega = c_1 \omega_1 + c_2 \omega_2, \tag{10.41}$$

c_1 and c_2 being constants. On substituting this value of Ω in (10.2) we find that

$$\{\varepsilon_1 - \varepsilon)\, c_1 + o\,(Z_{11} c_1 + Z_{12} c_2)\}\,\omega_1 + \{(\varepsilon_2 - \varepsilon)\, c_2 + o\,(Z_{21} c_1 + Z_{22} c_2)\}\,\omega_2 = 0,$$

where

$$\left.\begin{aligned} Z_{11} &= \left\{1 + \frac{\frac{1}{2}}{l + \frac{1}{2}}\right\}, \\ Z_{22} &= \left\{1 - \frac{\frac{1}{2}}{l + \frac{1}{2}}\right\}, \\ \text{and} \quad |Z_{12}| &= |Z_{21}| = \tfrac{1}{2}\left\{1 - \frac{u^2}{(l + \frac{1}{2})^2}\right\}^{\frac{1}{2}}. \end{aligned}\right\} \tag{10.42}$$

Since ω_1 and ω_2 are linearly independent it follows that

and
$$\left.\begin{aligned}(\varepsilon_1 - \varepsilon + oZ_{11})\,c_1 + oZ_{12}c_2 = 0,\\ oZ_{21}c_1 + (\varepsilon_2 - \varepsilon + oZ_{22})\,c_2 = 0.\end{aligned}\right\} \qquad (10.43)$$

To obtain the magnetic resolution with reference to the optical centre of ε_1 and ε_2 we express them by means of (8.33) in the form

where
$$\left.\begin{aligned}\varepsilon_1 = \varepsilon_c + \tfrac{1}{2}l\lambda \quad \text{and} \quad \varepsilon_2 = \varepsilon_c - \tfrac{1}{2}(l+1)\,\lambda,\\ \lambda = \frac{\delta}{l+\frac{1}{2}}.\end{aligned}\right\} \qquad (10.44)$$

We now eliminate the ratio $c_1 : c_2$ from equations (10.43) and introduce the values of Z_{ab} from (10.42) and the values of ε_1, ε_2 from (10.44). The final result is

$$\varepsilon - \varepsilon_c = uo - \tfrac{1}{4}\lambda \pm \tfrac{1}{2}(o^2 + 2ou\lambda + \delta^2)^{\frac{1}{2}}, \qquad (10.45)$$

in agreement with the formula of Voigt and Sommerfeld. Here and henceforward the upper and lower signs refer to the states with the larger and smaller inner quantum numbers respectively ($j = l \pm \frac{1}{2}$), as may be verified on putting o equal to zero and comparing equation (10.45) with (8.34).

If the magnetic field is "weak," *i.e.*, if the ratio o/δ is small,

$$\varepsilon - \varepsilon_c = \delta\gamma_w + oug_w, \qquad (10.51)$$

where

$$\gamma_w = \frac{j(j+1) - l(l+1) - \frac{3}{4}}{2(l+\frac{1}{2})} \text{ as in (8.35)}, \qquad (10.52)$$

and

$$g_w = 1 + \frac{j(j+1) - l(l+1) + \frac{3}{4}}{2j(j+1)}. \qquad (10.53)$$

These expressions for the Landé separation factors also hold in the case, $u = -l - \frac{1}{2}$, with the convention that $\delta = 0$.

If the magnetic field is "strong," *i.e.*, if the ratio o/δ is large,

$$\varepsilon - \varepsilon_c = \delta\gamma_s + oug_s, \qquad (10.61)$$

where

$$\gamma_s = \frac{\pm\frac{1}{2}u - \frac{1}{4}}{l+\frac{1}{2}}, \qquad (10.62)$$

and

$$g_s = 1 \pm \frac{1}{2u}. \qquad (10.63)$$

This expression for g_s does *not hold* in the case $u = -l - \frac{1}{2}$. In this case it follows from (10.32) that

$$g_s = -\frac{l+1}{u} = 1 - \frac{1}{2u}, \tag{10.64}$$

although $j - l$ is *plus* one-half.

§ 11. *The Paschen-Back Effect.*

In a "strong" magnetic field the possible transitions between energy levels are limited by another selection rule in addition to those obtained above, *i.e.*,

$$\Delta l = \pm 1, \qquad \Delta j = 0 \text{ or } \pm 1, \qquad \Delta u = 0 \text{ or } \pm 1.$$

This new rule arises from the fact that in a strong magnetic field Z behaves as a reducible operator.

If Ω is the ω-function for an atom in a strong field (10.41),

$$Z\,\Omega \sim c_1 (\omega_1 Z_{11} + \omega_2 Z_{21}) + c_2 (\omega_1 Z_{12} + \omega_2 Z_{22}),$$

by the expansion theorem of (7.4). We rewrite this expression as

$$\begin{aligned} &\omega_1 (Z_{11} c_1 + Z_{12} c_2) + \omega_2 (Z_{21} c_1 + Z_{22} c_2) \\ &\qquad = o^{-1} (\varepsilon - \varepsilon_1)\, c_1 \omega_1 + o^{-1} (\varepsilon - \varepsilon_2)\, c_2 \omega_2 \qquad (\text{from } (10.43)) \\ &\qquad \sim u g_s (c_1 \omega_1 + c_2 \omega_2), \quad \text{if } \delta/o \text{ is negligible.} \end{aligned}$$

Hence

$$Z\,\Omega \sim u g_s\, \Omega, \tag{11.1}$$

so that the Zeeman operator Z is reducible with eigen value $u g_s$.

Since, by equation (10.2)

$$Z \equiv \mathfrak{h}^{-1} M_3 + \tfrac{1}{2} S_3 = \mathfrak{h}^{-1} m_3 + S_3, \tag{11.2}$$

it follows that the operators $\frac{1}{2}S_3$ and m_3 are also both reducible. We now define the magnetic quantum numbers m_s and m_l by the equations

$$\left.\begin{aligned} \tfrac{1}{2} S_3 \,.\, \Omega &= m_s \Omega, \\ m_3 \,.\, \Omega &= m_l \mathfrak{h} \Omega, \end{aligned}\right\} \tag{11.3}$$

whence

$$u = m_l + m_s \tag{11.4}$$

Therefore, if

but, if

$$\left.\begin{array}{lll} u > -l - \tfrac{1}{2}, & m_s = \pm \tfrac{1}{2}, & \text{accordingly as } j = l \pm \tfrac{1}{2}, \\ u = -l - \tfrac{1}{2}, & m_s = -\tfrac{1}{2}, & \text{only, although } j = l + \tfrac{1}{2}. \end{array}\right\} \tag{11.5}$$

The general expressions for the separation factors in a strong field are

$$\gamma_s = \frac{m_l \, . \, m_s}{l + \frac{1}{2}}, \tag{11.6}$$

and

$$ug_s = u + m_s = m_l + 2m_s. \tag{11.7}$$

We note that the range of values of m_l is from $-l$ to $+l$ in integral steps.

The new selection rule is an immediate consequence of the reducibility of S_3. Since **x** and S_3 commute, it follows that the matrix element **x** (a, b) vanishes unless m_s has the same value in the states "*a*" and "*b*," *i.e.*,

$$\Delta m_s = 0. \tag{11.8}$$

This is the selection rule introduced by Pauli.* It follows that the changes in the energy levels are given by

$$\Delta \varepsilon \sim \Delta \varepsilon_c + o \Delta \, (ug_s) = \Delta \varepsilon_c + o \Delta u. \tag{11.9}$$

Since $\Delta u = \pm 1$ or zero, it follows that the spectral lines form a normal Zeeman triplet with intervals $o/h = e\mathrm{H}_3/4\pi m_0 c$.

* 'Z. Physik,' vol. 16, p. 155 (1923).

The Hyper-fine Structure of the Arc Spectrum, and the Nuclear Rotation of Indium.

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[Plate 6.]

Introductory.

The arc spectrum of indium was investigated with the object of finding whether any of its lines possessed hyperfine structure, resulting from a quantized nuclear spin, and a corresponding magnetic moment of the nucleus. The spectrum of cæsium,* which was investigated by the author, closely resembles that of indium, both spectra being peculiarly suitable for investigation in respect of hyperfine structure on account of their remarkable simplicity. In the case of cæsium it was found possible to resolve the structure arising from the S-levels, but not that due to the P-levels. In indium, however, it was hoped, on account of the far greater separation of the P-levels and the correspondingly greater interaction between the nuclear spin and the electron orbit, to achieve a resolution of the structure due to the P-levels. This was found possible. The apparatus used for high resolving power was a reflection echelon grating; the instrument was made of fused silica, platinized. It had 25 plates each 7 mm. thick. The grating was made by Adam Hilger, Ltd., and possessed its theoretical resolving power of about 800,000 at a wave-length of 4500 A.U. The mounting and method of using the echelon grating are fully described. The source of light was a cooled vacuum tube containing helium and indium chloride, excited with external electrodes by means of a high-frequency alternating current.

The analysis of the structure of the lines shows that the nucleus must be assumed to possess one quantum of rotation. The comparison of the deduced structures of the $P_{1/2}$ and the $P_{3/2}$ levels agrees quantitatively with Fermi's theory of the interaction of the nuclear and the electron spins.

Experimental—The Echelon Grating and its Mounting.

Until quite recently it had been considered impossible to construct a satisfactory reflecting echelon grating. For although it was possible to construct plates of sufficient accuracy for the construction of a transmission echelon grating, it was nevertheless not possible to use these for making a reflection echelon. The reason for this was the great difficulty in bringing the plates together without the inclusion of small particles of dust between the surfaces of contact. The effect of this on a transmission echelon is not harmful; but in the case of a reflecting echelon grating it would be sufficient to render the grating useless. By making the plates of fused silica Adam Hilger, Ltd., succeeded in overcoming this difficulty. The reflecting echelon grating possessed 25 plates, each plate being 7 mm. thick; the width and length of the steps were respectively 1 mm. and 40 mm. The advantages of this grating over a transmission grating are very great. In the first place the resolving power is at least four times as great as that of a transmission grating of similar dimensions. Secondly, the grating could be used in the extreme ultra-violet. Thirdly, owing to its being constructed of fused silica, changes in temperature are relatively harmless to the definition of photographs made with the instrument; which is of great importance when it is necessary to give long exposures.

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* 'Roy. Soc. Proc.,' A, vol. 121, p. 432 (1928).

The mounting of the reflecting echelon was of an entirely new design. As is well known, the echelon grating must be used in conjunction with an auxiliary spectroscope; the latter separates the lines of the spectrum under investigation, while the former reveals their fine structure. Numerous methods for doing this have been described, in the case of the transmission echelon; but these are not applicable to the reflecting echelon, owing to the fact that the light must return along the same path, in the opposite direction, as that along which it travels before striking the grating. Fig. 1 shows the form of mounting used. It can be seen that the mounting is of the Littrow type, and consequently possesses the advantages of compactness and rigidity and also the optical simplicity of this type of spectrograph. The mounting consists of a Littrow

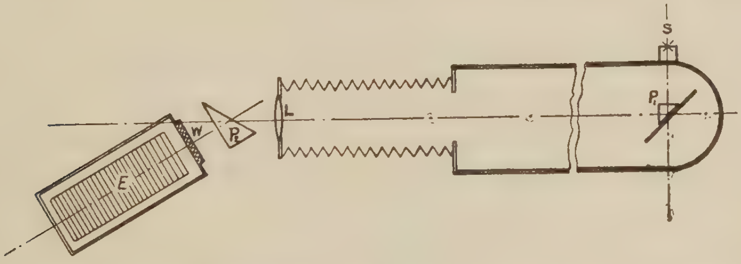

FIG. 1.—S, Crossed Slit; P_1, Reflecting Prism; P_2, 30° Quartz Prism; E, Echelon Grating in Brass Box with Quartz Window, W; L, Quartz Lens of 3 metres focus.

spectrograph with a 30° quartz prism; but instead of the back surface of the prism being silvered, it is left clear and the reflecting echelon grating is placed behind it. The steps of the grating are horizontal, and their surfaces are parallel to the back surface of the 30° prism. In addition to the usual vertical slit, the spectrograph has a horizontal cross slit. In this way a spectrum is obtained in which the dispersion due to the prism is crossed with the dispersion of the grating; the former being in a horizontal direction and the latter in a vertical direction.

The focus of the lens was made equal to 3 metres. This may at first seem surprisingly long; but even with this focus the distance between two successive orders—and consequently the width of the echelon spectrum—is at a wave-length of 4000 A.U. only 1 mm.; at shorter wave-lengths it is smaller than this, since it is proportional to the wave-length. If a shorter focus had been used the necessary length of exposures would have been reduced; but it would have been difficult to avoid loss of resolving power due to the size of the grain of the photographic plates used, and also the spreading of the image due to halation.

Another important character of the mounting is the enclosure of the grating in an air-tight box, fitted with a quartz window, and a device for adjusting the pressure of the air inside the box. This is introduced for a double purpose. In the first place, the grating being made of fused silica a change of temperature of as much as 5° would cause no appreciable loss in resolving power arising from expansion of the plates. But in order to gain the full advantage of this freedom from the influence of changes of temperature, it is necessary that the optical density of the air surrounding the grating remain constant. This is at once achieved by placing the grating in an air-tight box; for in this case the density of the air must remain the same; and if this condition is fulfilled the optical density also remains constant, even if the temperature, and consequently the pressure, of the air changes. With this arrangement, therefore, changes of less than 5° in temperature will not give rise to a serious loss in resolving power. If, however, the grating were not enclosed it would be necessary for the temperature of the air to remain constant to 1°, and the barometric pressure variation would have to be less than 3 mm. of mercury in order not to cause a loss of resolving power.

The second reason for enclosing the grating is the necessity of making slight alterations in the optical thickness of the plates. This change is equal approximately to one half-wave-length of light. In the case of the transmission grating it is achieved simply by tilting the grating slightly, when the effective thickness of the plates changes from $(\mu - 1)t$ to $(\mu - 1)t \sec \theta$. If this were to be done with the reflecting grating the spectrum would be moved right off the plate; so the change is effected by altering the density of the air surrounding the grating.

This change is necessary on account of the fact that the apparent intensity of a line in the echelon spectrum is a function of its wave-length and the thickness of the plates. If this is such that $n \,.\, \lambda = 2\mu_1 t$ the line is visible in one strong order and has the maximum intensity. If, however, the wave-length is such that $n\lambda + \frac{1}{2}\lambda = 2\mu_2 t$ the line is visible in two orders of equal intensity, and of minimum value; the intensity being only one-third of that in the single-order position. The relation between the apparent intensity of a line and its wave-length and the thickness of the plates is in fact given by the equation

$$\mathrm{I} = \mathrm{I}_0 \sin^2\left(\pi \frac{s}{\lambda} \,.\, \theta\right) \Big/ \left(\pi \frac{s}{\lambda} \theta\right)^2,$$

where s = width of echelon step, θ = angle of diffraction, λ = wave-length of light.

This can also be expressed as

$$\mathrm{I} = \mathrm{I}_0 \sin^2\left(\pi \frac{d\lambda}{\lambda}\right) \Big/ \left(\pi \frac{d\lambda}{\lambda}\right)^2,$$

in which $d\lambda$ is given by the equation $n\lambda + d\lambda = 2\mu t$, where μ = refractive index of air surrounding echelon, t = thickness of echelon plate. In order, therefore, to observe satisfactorily the relative intensities of the lines composing the fine structure it is desirable to take two photographs in which the density of the air surrounding the echelon differs in such a way that

$$2\mu_1 t - 2\mu_2 t = \tfrac{1}{2}\lambda,$$

where μ_1 = refractive index of air for first exposure, μ_2 = refractive index of air for second exposure, t = thickness of echelon plate. When this is done the lines of maximum apparent intensity in the first photograph will be in the position of minimum apparent intensity in the second photograph, and *vice versa*; and it is a very much simpler matter to form an estimate of the intensities of the lines when two such photographs can be compared. The required values of μ_1 and μ_2 are given by the equation

$$\mu_1 - \mu_2 = \lambda/4t.$$

From the known values of the refractive index of air, the values of the difference in density required can be calculated; or, if the temperature of the air remains

Table I.

Wave-length.	Pressure change at 15°.	Wave-length.	Pressure change at 15°.
A.U.	cm.	A.U.	cm.
2000	1·67	5000	4·88
2500	2·26	5500	5·38
3000	2·80	6000	5·88
3500	3·35	6500	6·42
4000	3·78	7000	6·94
4500	4·38	7500	7·42

constant, the corresponding change in pressure. The accompanying table gives the change in pressure required at a temperature of 15°. The change at other temperatures is

$$\Delta P_\theta = \Delta P_{15} \, . \, \theta/288,$$

where ΔP_{15} = change at 15°, ΔP_θ = change at θ°.

The accompanying graph (fig. 2) shows the relative intensities of a line for various values of the fraction $d\lambda/\lambda$. In the single-order position, where $d\lambda/\lambda = 0$, the intensity is called 1. In any other position a line is visible in two orders of the intensity shown in the graph. The minimum value, of course, corresponds to the fraction $d\lambda/\lambda$ being equal to $\frac{1}{2}$. Here the line is visible in two orders of equal intensity ; this intensity being equal to 0·4, if 1 is that in the single-order position. In any other position there are two orders visible, one of intensity greater than 0·4 and one of intensity less than this. The single-order position may be regarded as the extreme case of this.

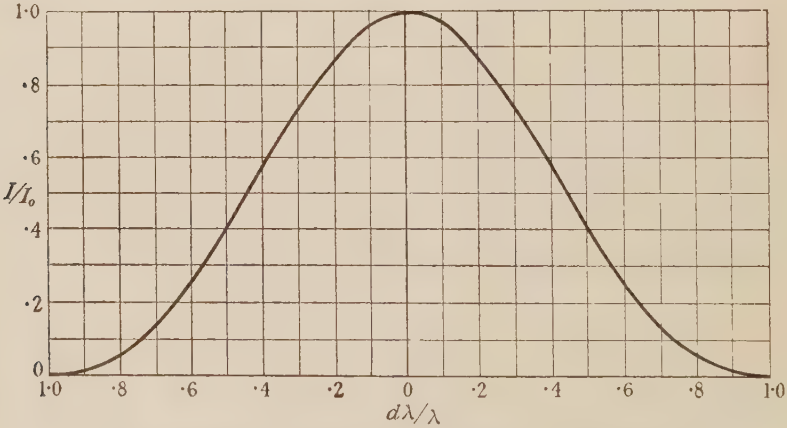

Fig. 2.—Distribution of Intensity in Echelon Grating Spectrum.

Experimental—Method of Exciting Spectrum.

In order to obtain a source of light suitable for the study of fine structure three conditions must be fulfilled. The vapour pressure of the substance, the spectrum of which is being investigated, must be sufficiently low to ensure that no self-reversal or broadening of the lines takes place. Secondly, the temperature of the vapour must be as low as possible in order to reduce the natural width of the lines due to the Doppler effect to a minimum. Finally the vapour must not be subjected to any strong electric fields, which are likely to broaden the lines by giving rise to a Stark effect. The first and the last of these three conditions can be fulfilled by using as a light source a discharge tube filled with helium at a few millimetres' pressure, and containing a small quantity of the vapour of the metal whose spectrum is required. The temperature of the tube is then adjusted so that the vapour pressure of the metal is of the order of one-hundredth of a millimetre. If the tube is excited the spectrum shows the lines of the metal and of helium in about the same intensity. Under these conditions the vapour pressure of the metal is sufficiently low to remove any possibility of self-reversal or broadening, while owing to the high conductivity of the helium there is no danger of the presence of strong electric fields. The width of the lines is in fact no greater than that corresponding to the Doppler-effect blurring of the lines at the temperature of the emitting atoms ; that is to say, the temperature at which the metal under investigation has a vapour pressure of about one-hundredth of a millimetre. With readily volatile metals for which such a pressure is reached between 100° and 200° very sharp lines can be obtained by this method of excitation. Thus in the case of cæsium, which has the necessary vapour pressure at a temperature of about 140°, the method can be used very satisfactorily. But for indium a new method had to be found. For this metal is very unvolatile and would have to be heated to a temperature of about 800° in order to have a sufficiently high vapour pressure to give reasonably strong lines. And at this temperature the Doppler effect would set an upper limit of less than 400,000 on the resolving power which could be achieved. This difficulty was overcome by using the trichloride of the metal instead of the metal itself. This compound is very much more volatile than indium, and has in fact a sufficiently high vapour pressure at about 150° to bring out the metal lines strongly in a helium tube. The discharge tubes were of the electrodeless type ; they were made of fused silica, the ends being about 7 cm. long and 4 cm. in diameter, and the capillary portion about 5 cm. long and about 6 mm. internal diameter. Three distilling bulbs were connected on to the tube, so that the indium trichloride to be introduced could be redistilled three times. When the compound had been distilled in, the tube was filled with helium at a pressure of about 1 mm. and sealed off. The indium chloride was then brought in to the capillary portion of the tube. The method of excitation was by means of a high-frequency oscillator connected to large copper external electrodes which were wrapped round the ends of the discharge tube. The oscillator was of the type described by Gutton*; two ¼-K.W. 2000-volt triode valves being used. The heat generated by the passage of the discharge in the tube volatilizes the indium chloride. In order to prevent the vapour pressure of the indium chloride from becoming too high, the tube was cooled by means of a fan. The temperature of the tube was so adjusted that the vapour pressure of the indium chloride was sufficiently great to make the intensity of the indium 4511 line equal to that of the helium 4471 line. This was controlled by observation with a direct-vision spectroscope. Under these conditions the yellow helium discharge had a faint purple tinge, and the lines of the indium spectrum were quite free from self-reversal, or broadening. If the tube was allowed to become hotter the indium lines became stronger, and the discharge became blue in colour; but the indium lines became broadened or even self-reversed. If, however, the tube was kept sufficiently cool, in the manner described above, there was no trouble in getting the lines very fine and perfectly free from any self-reversal or broadening.

The lines observed were the two resonance lines $2\,{}^2P_{1/2} - 2\,S_{1/2}$ and $2\,{}^2P_{3/2} - 2\,S_{1/2}$ and the first three lines of the diffuse series, $2\,{}^2P_{3/2} - 3\,{}^2D_{5/2}$, $2\,{}^2P_{3/2} - 3\,{}^2D_{3/2}$ and $2\,{}^2P_{1/2} - 3\,{}^2D_{3/2}$. Some of the higher lines were also investigated, but on account of the relatively greater effect of the Doppler effect on the width of a line of shorter wave-length (the width being measured in frequency units) the definition was not satisfactory. The five measured lines are shown in the accompanying photograph (Plate 6). The echelon spectra of the two resonance lines are also crossed with Fabry and Perot interference fringes; fringes made by a 2½-mm. etalon being projected by means of a 15-cm. objective on to the spectrograph slit. The crossing of the echelon spectrum with interference fringes served a double purpose; first to reveal the possible presence of ghosts (these are proved to be absent), and secondly to establish which lines of the echelon spectrum are in the same order of spectrum. The necessity of this is very apparent in the case of the line 4101. The interference fringes show very clearly that the two very close strong lines are not in the same order, but are in adjacent orders; the true structure of the

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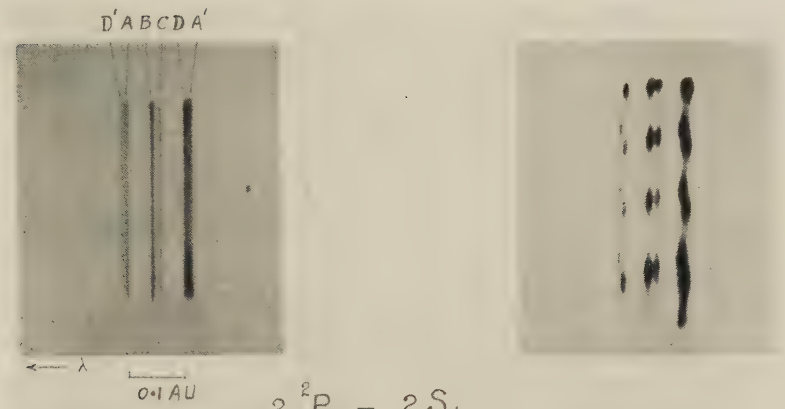
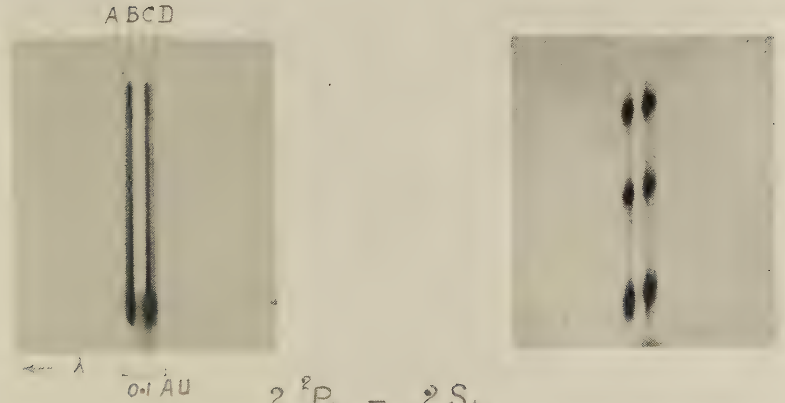
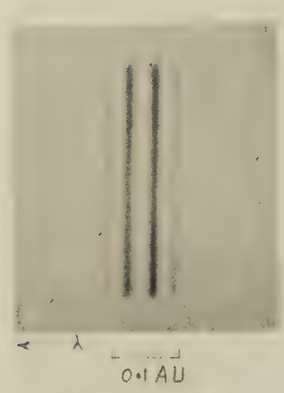
* 'Oude Electrique,' vol. 4, p. 387 (1925).


D'ABCDA'
← λ
0·1 AU

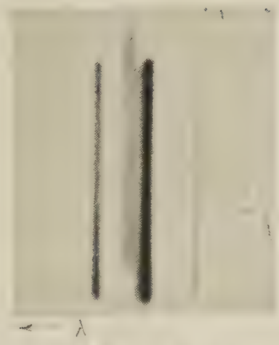
$2\,^2P_{1/2} - 2\,S_{1/2}$



$2\,^2P_{3/2} - 2\,S_{1/2}$



$2\,^2P_{1/2} - 3\,^2D_{3/2}$



$2\,^2P_{3/2} - 3\,^2D_{3/2}$

$2\,^2P_{3/2} - 3\,^2D_{5/2}$

(*Facing p.* 514.)

[For Plate 6 in text *read* Plate 6A.]

line being ABCD and not D′ABC as might otherwise have been supposed. The fine structure of the line 4511, on the other hand, extends over a very much narrower spectral range, and the lines are all in the same order. All the spectra were measured on five independent plates, each plate being measured three times. The accuracy of measurement is very great, on account of the very high resolving power and dispersion of the spectrograms. The scale of the original plates is somewhat greater than 10 mm. to the Angstrom unit. The accuracy with which these lines could be measured varies from about 0·002 mm. in the most favourable case to about 0·005 in the least favourable lines. The accuracy is probably increased slightly by the multiple measurement. An estimate of the accuracy in A.U. and cm.$^{-1}$ is given for each line in the table of results. The reproduced photograph is enlarged about seven times from the original scale.

$2\,^2P_{1/2} - 2\,S_{1/2}$. 4101.

This line was found to possess four components, all of which can be seen clearly in the reproduced photograph. The lines are given in order of increasing wave-number, and the letters refer to the identification letters on the photograph. The accuracy of measurement is about 0·002 mm., corresponding to 0·002 cm.$^{-1}$ or 0·0004 A.U.

Line.	Intensity.	Separation, A.U.	Separation, cm.$^{-1}$.
A	10	0·0000	0·0000
B	6	0·0472	0·281
C	3	0·0638	0·380
D	10	0·1106	0·658

The following constant frequency differences are apparent :—

$$C - A = 0{\cdot}380\ ;\ \ D - B = 0{\cdot}377, \text{ average } 0{\cdot}379.$$

$$B - A = 0{\cdot}281\ ;\ \ D - C = 0{\cdot}278, \text{ average } 0{\cdot}279.$$

$2\,^2P_{3/2} - 2\,S_{1/2}$. 4511.

This line also possesses four components, consisting of two very close doublets. The longer wave-length pair is only just resolved, the weaker component appearing as a shading on the long wave-length side, just separated from the stronger line. The very small separation of these lines considerably increased the difficulty of measurement ; the accuracy is probably about half as great as for the 4101 line ; that is, about 0·004 mm., corresponding to 0·005 cm.$^{-1}$ or 0·001 A.U.

Line.	Intensity.	Separation, A.U.	Separation, cm.$^{-1}$.
A	4	0·0000	0·000
B	10	0·0092	0·045
C	10	0·0415	0·204
D	4	0·0562	0·276

The following frequency differences are of interest :—

$$D - A = 0{\cdot}276 ; \quad B - A = 0{\cdot}045 ; \quad D - C = 0{\cdot}072.$$

$2\,{}^2P_{1/2} - 3\,{}^2D_{3/2}$. 3039.

This line was found to be a doublet with components of approximately equal intensity. The separation of the two lines is 0·389 cm.$^{-1}$. The accuracy of measurement is about 0·005 cm.$^{-1}$.

$2\,{}^2P_{3/2} - 3\,{}^2D_{5/2}$, 3256, *and* $2\,{}^2P_{3/2} - 3\,{}^2D_{3/2}$, 3259.

As can be seen from the photograph, the structure of these lines cannot be resolved. It is interesting, however, to note that the width of the unresolved pattern $2\,{}^2P_{3/2} - 3\,{}^2D_{3/2}$, 3259, is about 0·13 cm.$^{-1}$. This agrees very satisfactorily with the sum of the separations between the very close doublets of the line 0000, this quantity being equal to 0·12 cm.$^{-1}$.

Theoretical Discussion.

The hyperfine structure of the spectrum of bismuth has been accounted for by Back and Goudsmid* by assuming a quantized nuclear spin ; and in the spectrum of cæsium the author† was able to explain in an approximate way the quantitative magnetic moment of the nucleus (arising from the nuclear spin) required to give the experimentally observed fine structure of the lines of the principal series. The former work suffers from the defect that only one line was systematically observed ; and also the theoretical discussion is rendered more difficult by the complicated nature of the spectrum. The latter suffers from the serious defect that the structure of the P levels could not be directly observed, but had to be deduced from the difference in the separations of the fine structure doublets in the $S_{1/2} - {}^2P_{3/2}$ and the $S_{1/2} - {}^2P_{1/2}$ lines. It has, however, the advantage of the extreme simplicity of the cæsium arc spectrum, which rendered the formation of theoretical conclusions very much simpler.

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* 'Z. Physik,' vol. 47, p. 174 (1928).

† *Loc. cit.*, p. 440.

The indium spectrum combines the advantages of complete resolution of the structure as in the case of the bismuth line, and simplicity of the spectrum, as in the case of cæsium, whilst permitting a more extensive examination of the lines. The greater separation of the structure of the P levels in indium was to be expected from the conclusion that the hyperfine structure separation of homologous lines is very roughly proportional to the multiplett separation. Analysis of the fine structure of the lines $2\,^2P_{1/2} - 2\,S_{1/2}$, $2\,^2P_{3/2} - 2\,^2S_{1/2}$ and $2\,^2P_{1/2} - 3\,^2D_{3/2}$, gave the fine structure energy levels of the S level and the two P levels. Firstly the line 4101 was resolved into four components; these four lines can be represented by transitions between two double levels, the separations of which are respectively 0·379 cm.$^{-1}$ and 0·279 cm.$^{-1}$. Now the separation 0·379 corresponds very nearly to the value 0·389, the separation of the two fine structure components of the line $2\,^2P_{1/2} - 3\,^2D_{3/2}$; it may, therefore, be safely ascribed to the $2\,^2P_{1/2}$ level.

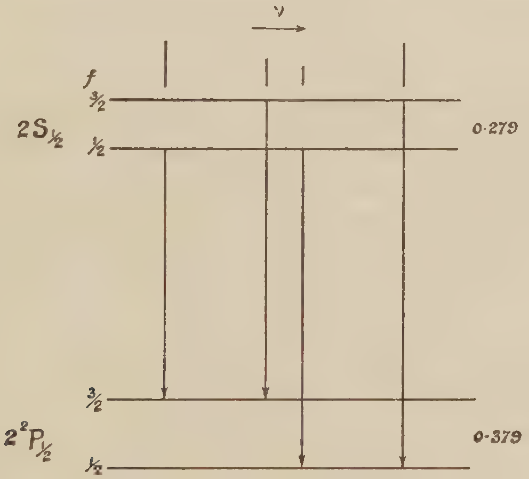

FIG. 3.—$2\,^2P_{1/2} - 2\,S_{1/2}$. 4101.

In the accompanying energy diagram the quantum number *f* corresponds to the vectorial sum of *i* and *j*; *i* is the quantum number of the quantized nuclear spin, and *j* is the usual "inner quantum number" given by the vectorial addition of *l* and *s*, the quantum numbers associated with the electron rotation and the electron spin respectively. From this energy diagram alone it is not possible to fix the value of *i*; it can only be stated that it must be greater than one-half, on account of the presence of the weakest line, which would correspond to the transition 0 — 0; and this transition is in all probability forbidden; on the other hand the weakness of this line indicates that the value of *i* cannot be very great. For reasons explained later in connection with the structure of the line $2\,^2P_{3/2} - 2\,S_{1/2}$ it appears that the most probable value of *i* is one; and this value is therefore given in the diagram.

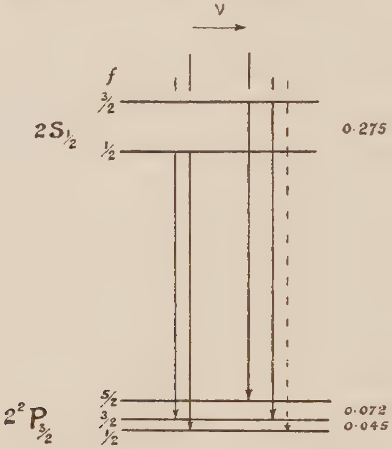

FIG. 4.—$2\,^2P_{3/2} - 2\,S_{1/2}$. 4511.

The structure of the line 3039, $2\,^2P_{1/2} - 3\,^2D_{3/2}$ is, as already stated, a simple doublet. This is at once explained by ascribing to the $2\,^2P_{1/2}$ level the same doublet structure as in the case of the 4101 line. The small discrepancy of 0·01 cm.$^{-1}$ is within the experimental error. The $3\,^2D_{3/2}$ level is assumed to be simple; or better, the spacing of the structure is so small as to be quite unobservable. This is to be expected on the view that hyperfine structure separation and multiplett structure separation are roughly proportional. For the D level separations are about 100 times smaller than the P level separation; so that the separation of the hyperfine structure levels of the D levels would be of the order of 0·004 cm.$^{-1}$; that is to say, far beyond the possibility of resolution.

The line 4511, $2\,^2P_{3/2} - 2\,S_{1/2}$ possesses four components; but these cannot be represented by transitions between two doublet levels, as could be done for the line 4101. Nevertheless the separation 0·276 cm.$^{-1}$ corresponds very well to the S level separation. The line is therefore represented as arising from transitions between a doublet S level and a triplet P level. The separations of the P levels are 0·072 cm.$^{-1}$ and 0·045 cm.$^{-1}$ respectively. It might be expected from this diagram that the structure would contain five lines, the fifth line corresponding to the transition represented by the dotted arrow in the energy diagram. This could not be observed. The reason for the absence of this line is difficult to find. The line should certainly be very much weaker than the others, but it is surprising that it should be completely missing. The triplet structure of the $2\,{}^2P_{3/2}$ level can be explained only by ascribing the value one to the quantum number i of the nuclear spin. The ratio of the separations between these three levels is of great interest, as it gives further evidence in favour of the assumption that the value of i is one. The origin of the hyperfine structure being regarded as the interaction of the nuclear magnetic moment (caused by the quantized nuclear spin) and the rotation of the electron in its orbit, the effect that it has on the energy of an orbit will be*

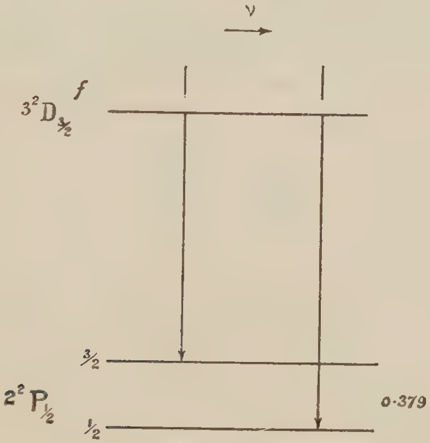

FIG. 5.—$2\,{}^2P_{1/2} - 3\,{}^2D_{3/2}$. 3039.

$$\begin{aligned} E\,(i, j) &= a\,.\,i\,.\,j\,(\cos i, j) \\ &= \tfrac{1}{2}a\,\{f(f+1) - j(j+1) - i(i+1)\}, \end{aligned}$$

so that the differences in energy between the levels $f = 5/2$ and $f = 3/2$, and $f = 3/2$ and $f = 1/2$, are :—

$$E\,(1, 5/2) - E\,(1, 3/2) = \frac{a}{2}\left(\frac{5}{2}\cdot\frac{7}{2} - \frac{3}{2}\cdot\frac{5}{2}\right) = \frac{5}{2}\,.\,a,$$

$$E\,(1, 3/2) - E\,(1, 1/2) = \frac{a}{2}\left(\frac{3}{2}\cdot\frac{5}{2} - \frac{1}{2}\cdot\frac{3}{2}\right) = \frac{3}{2}\,.\,a.$$

The ratio of these differences should therefore be, if i is assumed to be one, exactly 5 : 3. The values actually observed are 0·072 : 0·045. This is in almost perfect agreement, the total error being only 0·003 cm.$^{-1}$, which is well within the experimental error.

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* Back and Goudsmid, 'Z. Physik,' vol. 47, p. 176 (1928).

It is thus fairly well established that the quantized nuclear rotation has the value one.

Another very interesting point is the relation between the hyperfine structure of the $2\,{}^2P_{1/2}$ level and that of the $2\,{}^2P_{3/2}$ level. The separation between the two levels comprising the $2\,{}^2P_{1/2}$ level is 0·38 cm.$^{-1}$, while the separation between the highest and lowest levels of the $2\,{}^2P_{3/2}$ level is 0·12 cm.$^{-1}$. On the view that the hyperfine structure arises from the interaction of the nuclear spin and the rotation of the electron these two quantities would have to be very nearly equal. For it has been shown by the author* that

$$\frac{\Delta N_\kappa}{\Delta N_e} = \frac{1}{\frac{1}{2}Z} \cdot \frac{M_\kappa}{M_e},$$

where ΔN_κ = separation between P level hyperfine structure levels, these being assumed equal, ΔN_e = separation between the P multiplett levels, M_κ = magnetic moment of nucleus, M_e = magnetic moment of electron spin.

The experimental evidence for the indium P levels cannot be reconciled with this simple theory ; for here the two P level fine structure separations are by no means equal. The reason for this is at once given by a work of Fermi.† He points out that the simple theory suffers from the fault that only the interaction between the nuclear spin and the electron rotation is considered, the interaction between the electron spin and the nuclear spin being neglected. Taking this into consideration, Fermi recalculated the whole problem, using wave-mechanical methods. This proved that the hyperfine structure for the two P levels should be different ; that for the $2\,{}^2P_{1/2}$ level being nearly twice as great as that given by the simple theory; whereas for the $2\,{}^2P_{3/2}$ level the value is decidedly smaller. The actual values are

$$\frac{\Delta\,({}^2P_{1/2})}{\Delta N_e} = \frac{32}{9} \cdot \frac{1}{Z} \cdot \frac{M_\kappa}{M_e} \quad \text{and} \quad \frac{\Delta\,({}^2P_{3/2})}{\Delta N_e} = \frac{64}{45} \cdot \frac{1}{Z} \cdot \frac{M_\kappa}{M_e}.$$

According to this theory, therefore, the separations of the two $2\,{}^2P_{1/2}$ levels and the separation of the highest and lowest levels of the $2\,{}^2P_{3/2}$ levels should be in the ratio of 32/9 : 64/45 ; that is, 2·8 : 1. The actual observed value is 0·38 : 0·12, which is equal to 3·2 : 1. This is within the limits of experimental error; for the figure $0 \cdot 12$ for the $2\,{}^2P_{3/2}$ level is obtained by adding two frequency differences each of which may be in error to the extent of $0 \cdot 005$ cm.$^{-1}$. Alternatively the value $0 \cdot 13$, from measurement of the width of the unresolved group $2\,{}^2P_{3/2} - 3\,{}^2D_{3/2}$, can be taken. This gives the value $2 \cdot 9 : 1$ for the ratio, the agreement being still better. The comparison with these results gives, therefore, very strong experimental support to Fermi's more accurate theory. The value of the magnetic moment of the nucleus can be calculated approximately by means of the simple theory, but more exactly by Fermi's theory. This gives as the ratio of magnetic moment of the nucleus to the magnetic moment of the electron

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* *Loc. cit.*, p. 464.

† ‘Z. Physik,’ vol. 60, p. 320 (1930).

$$\frac{M_\kappa}{M_e} = \frac{\Delta\,({}^2P_{1/2})}{\Delta N_e} \,.\, Z \,.\, \frac{9}{32} = \frac{0 \cdot 379}{2212} \,.\, 49 \,.\, \frac{9}{32} = 2 \cdot 37 \times 10^{-3} \quad \text{or} \quad \frac{4 \cdot 36}{1840}.$$

If the distribution of mass and charge were the same in the nucleus as in the electron the ratio would be

$$2 \,.\, \frac{49}{115} \,.\, \frac{1}{1840} = \frac{0 \cdot 9}{1840}$$

(the factor 2 arising from the whole quantum spin of the nucleus as compared to the half quantum of the electron, whilst the factor $\frac{49}{115} \,.\, \frac{1}{1840}$ represents the ratio of charge over mass for the indium nucleus to charge over mass of the electron). The value found is thus about five times too great. It is of interest to compare this with the value found by the author* for the cæsium nucleus. This was equal to $\frac{1}{2}Z/55{,}000$ or $0 \cdot 9 : 1840$; the value expected here (the nucleus being assumed to have one-half quantum of rotation) was $55/132 : 1840$, or $0 \cdot 4 : 1840$. Two possible explanations of the too great value of the magnetic moment of the cæsium nucleus were given. The first of these was that the nucleus possesses more than a half quantum of spin; the second was that the excess positive charge of the nucleus is situated on the average nearer to the periphery than the centre, thus giving rise to a greater ratio of magnetic to mechanical moment. But in the case of indium the first explanation cannot be invoked; for it was proved fairly conclusively that the number of quanta of spin is one. The second explanation, therefore, appears to be the only tenable one. It is satisfactory to note, however, that the ratio is of the same order of magnitude as that calculated, and it is proved that the magnetic moment cannot arise from an unbalanced spinning electron in the nucleus; for this would possess a magnetic moment several thousand times greater than that deduced from the hyperfine structure.

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* *Loc. cit.*, p. 445.

† This value of the magnetic moment of the nucleus was found by the simple theory, neglecting the interaction of the electron spin. The error introduced by this is not very serious. For it was assumed that the separations of both the P level were equal; and since according to Fermi's theory that of the ${}^2P_{1/2}$ level is very much greater than that of the ${}^2P_{3/2}$ level, the value for the ${}^2P_{1/2}$ level is very nearly twice as great as that assumed. On the other hand, my formula for the magnetic moment of the nucleus, when applied to the ${}^2P_{1/2}$ level, gives a value very nearly twice too great; so that the two errors approximately cancel each other.

The conclusions formed from the theoretical consideration of the hyperfine structure of the lines of the arc spectrum of indium are therefore :—

1. The structure of the energy levels can be explained quantitatively by ascribing one quantum of rotation to the nucleus.
2. The value of the magnetic moment of the indium nucleus is about 5/1840 of that of a spinning electron, or about five times as great as that found for cæsium.
3. The comparison of the fine structure of the $2\,{}^2P_{1/2}$ and the $2\,{}^2P_{3/2}$ levels gives a very accurate quantitative proof of Fermi's wave-mechanical calculation of the interaction of electron spin and nuclear spin.

The author takes this opportunity for expressing his thanks to Prof. Lindemann for the encouragement and advice which he gave throughout the course of this research.

A General Solution of Einstein's Equations for Systems Involving Three Variables.

By W. R. ANDRESS, B.A., B.Sc.

(Communicated by Sir Arthur Eddington, F.R.S.—Received May 24, 1930.)

§ 1. In this paper we produce and discuss some general solutions of Einstein's gravitational equations. For simplicity we restrict the group of solutions to those which involve only three of the space-time variables explicitly. It is immaterial which co-ordinate does not occur explicitly as we can, by transformation and appropriate boundary conditions, choose this co-ordinate to be whichever is desired. The transformation may be an imaginary one, but in the analysis no reality conditions are implied, so that choice of the time co-ordinate is purely a matter of the physical interpretation of the final results.

We consider first the Cartesian ground-form in completely empty space, and modify it by the introduction of exponential factors, thus

$$ds^2 = - e^{\lambda} \, dx^2 - e^{\mu} \, dy^2 - e^{\nu} \, dz^2 + e^{\rho} \, dt^2, \tag{1.0}$$

where λ, μ, ν, ρ are to be explicit functions of (x, y, z). This ground-form is to be thought of as a Cartesian ground-form in empty space which has been perturbed by the presence of the non-vanishing functions λ, μ, ν, ρ, and we endeavour to interpret this perturbation as the result of the introduction of matter into the previously empty world. This interpretation may be permissible provided the components of the contracted Riemann tensor $G_{\mu\nu}$, vanish at all points unoccupied by matter, and that the necessary boundary conditions and continuity also obtain. These equations $G_{\mu\nu} = 0$ are then solved for λ, μ, ν, ρ. By regarding λ, μ, ν, ρ as perturbations it is not unreasonable to attempt to solve the gravitational equations, by a series of successive approximations, to be determined by selecting the terms in succession, according to their weight in λ, μ, ν, ρ.

The solution of the linear terms gives immediately, as an arbitrary function of integration, a function $\sigma(x, y, z)$ which is afterwards referred to as the auxiliary density distribution of the matter. The generality of the method lies in the fact that $\sigma(x, y, z)$ is entirely arbitrary. $\sigma(x, y, z)$ is the first order approximation to the actual distribution of the matter present, and it is as a series of successive orders in $\sigma(x, y, z)$ that the solutions for λ, μ, ν, ρ are finally expressed.

It is of importance that the ground-form (1.0) even after perturbation remains an orthogonal form, so that *a priori* there is no guarantee that solutions can be found (other than λ, μ, ν, ρ all vanishing). This is due to the fact that there are seven equations which have to be satisfied by four functions λ, μ, ν, ρ. The vanishing of divergence of the energy tensor gives

$$\frac{\partial \mathfrak{T}_{\nu}^{\mu}}{\partial x_{\mu}} = -\{\mu, \nu, \sigma\}\, \mathfrak{T}_{\sigma}^{\mu}. \qquad (1.1)$$

That is, three linear differential relations between the seven equations $G_{\mu\nu} = 0$. The main theorem that all the seven equations $G_{\mu\nu} = 0$ can be simultaneously satisfied, without any arbitrary functions of integration, really depends upon the fact, that under the special conditions of the problem, three integrals of the equations (1.1) can be found which do not involve any arbitrary functions other than $\sigma(x, y, z)$.

Since the solutions for λ, μ, ν, ρ are convergent for $\sigma(x, y, z) = 0$, it is to be expected that for sufficiently small values of $\sigma(x, y, z)$, the solutions retain convergence. Further, for small $\sigma(x, y, z)$ the solution agrees with that given by the Newtonian mechanics, to which, in turn, the relativity solution approximates.

The process of the calculation of the distribution of matter and the stresses present may be carried out as in a previous paper,* and as previously, when considering distributions of higher order than the first, we must be content with the values of the integrals taken over surfaces, which may enclose, but must not cut, the matter present.

The method developed is of fairly wide generality, as a large number of problems are reducible to three-variable considerations, and although the perturbed form is orthogonal, $\sigma(x, y, z)$ is entirely arbitrary. It does not seem to be readily extensible to four-variable problems.

§ 2. Consider the ground-form

$$ds^2 = -e^{\lambda}\, dx^2 - e^{\mu}\, dy^2 - e^{\nu}\, dz^2 + e^{\rho}\, dt, \qquad (2.0)$$

where λ, μ, ν, ρ are functions of x, y, z. If we denote partial differentiation with respect to x, y, z by suffixes 1, 2, 3 respectively and $\omega \equiv \lambda + \mu + \nu + \rho$, the evaluation of the components of the contracted Riemann tensor by means of the usual formula,

$$G_{\mu\nu} = -\frac{\partial}{\partial x_{\alpha}}\{\mu\nu, \alpha\} + \{\mu\alpha, \beta\}\{\nu\beta, \alpha\}$$
$$+ \frac{\partial^2}{\partial x_{\mu}\, \partial x_{\nu}} \log\sqrt{(-g)} - \{\mu\nu, \alpha\}\frac{\partial}{\partial x_{\alpha}} \log\sqrt{(-g)}$$

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* 'Proc. Roy. Soc.,' vol. 126, p. 592 (1930).

yields only seven distinct components which have the following values :—

$$G_{11} = \tfrac{1}{2}(\mu_{11} + \nu_{11} + \rho_{11}) + \tfrac{1}{2}e^{\lambda-\mu}\{\lambda_{22} + \tfrac{1}{2}\lambda_2(\omega_2 - 2\mu_2)\}$$
$$+ \tfrac{1}{2}e^{\lambda-\nu}\{\lambda_{33} + \tfrac{1}{2}\lambda_3(\omega_3 - 2\nu_3)\} + \tfrac{1}{4}(\lambda_1^2 + \mu_1^2 + \nu_1^2 + \rho_1^2 - \lambda_1\omega_1).$$

$$G_{22} = \tfrac{1}{2}(\lambda_{22} + \nu_{22} + \rho_{22}) + \tfrac{1}{2}e^{\mu-\lambda}\{\mu_{11} + \tfrac{1}{2}\mu_1(\omega_1 - 2\lambda_1)\}$$
$$+ \tfrac{1}{2}e^{\mu-\lambda}\{\mu_{33} + \tfrac{1}{2}\mu_3(\omega_3 - 2\nu_3)\} + \tfrac{1}{4}(\lambda_2^2 + \mu_2^2 + \nu_2^2 + \rho_2^2 - \mu_2\omega_2).$$

$$G_{33} = \tfrac{1}{2}(\lambda_{33} + \mu_{33} + \rho_{33}) + \tfrac{1}{2}e^{\nu-\lambda}\{\nu_{11} + \tfrac{1}{2}\nu_1(\omega_1 - 2\lambda_1)\}$$
$$+ \tfrac{1}{2}e^{\nu-\mu}\{\nu_{22} + \tfrac{1}{2}\nu_2(\omega_2 - 2\mu_2)\} + \tfrac{1}{4}(\lambda_3^2 + \mu_3^2 + \nu_3^2 + \rho_3^2 - \nu_3\omega_3),$$

$$G_{44} = -\tfrac{1}{2}e^{\rho-\lambda}\{\rho_{11} + \tfrac{1}{2}\rho_1(\omega_1 - 2\lambda_1)\} - \tfrac{1}{2}e^{\rho-\mu}\{\rho_{22} + \tfrac{1}{2}\rho_2(\omega_2 - 2\mu_2)\}$$
$$- \tfrac{1}{2}e^{\rho-\nu}\{\rho_{33} + \tfrac{1}{2}\rho_3(\omega_3 - 2\nu_3)\},$$

$$G_{12} = \tfrac{1}{2}(\nu_{12} + \rho_{12}) + \tfrac{1}{4}(\lambda_1\lambda_2 + \mu_1\mu_2 + \nu_1\nu_2 + \rho_1\rho_2 + 2\lambda_2\mu_1 - \lambda_2\omega_1 - \mu_1\omega_2),$$

$$G_{23} = \tfrac{1}{2}(\lambda_{23} + \rho_{23}) + \tfrac{1}{4}(\lambda_2\lambda_3 + \mu_2\mu_3 + \nu_2\nu_3 + \rho_2\rho_3 + 2\nu_2\mu_3 - \mu_3\omega_2 - \nu_2\omega_3),$$

$$G_{31} = \tfrac{1}{2}(\mu_{31} + \rho_{31}) + \tfrac{1}{4}(\lambda_3\lambda_1 + \mu_3\mu_1 + \nu_3\nu_1 + \rho_3\rho_1 + 2\lambda_3\nu_1 - \lambda_3\omega_1 - \nu_1\omega_3). \tag{2.1}$$

We proceed to solve the equation $G_{\mu\nu} = 0$ for λ, μ, ν, ρ by successive approximation, and first select the linear terms which are :—

$$\left.\begin{aligned} 2G_{11}^{(1)} &= \mu_{11} + \nu_{11} + \rho_{11} + \lambda_{22} + \lambda_{33} = 0 \\ 2G_{22}^{(1)} &= \lambda_{22} + \nu_{22} + \rho_{22} + \mu_{11} + \mu_{33} = 0 \\ 2G_{33}^{(1)} &= \lambda_{33} + \mu_{33} + \rho_{33} + \nu_{11} + \nu_{22} = 0 \end{aligned}\right\}, \tag{2.21}$$

$$-2G_{44}^{(1)} = \rho_{11} + \rho_{22} + \rho_{33} = 0, \tag{2.22}$$

$$\left.\begin{aligned} 2G_{12}^{(1)} &= \nu_{12} + \rho_{12} = 0 \\ 2G_{23}^{(1)} &= \lambda_{23} + \rho_{23} = 0 \\ 2G_{31}^{(1)} &= \mu_{31} + \rho_{31} = 0 \end{aligned}\right\}. \tag{2.23}$$

Where the upper suffix indicates the order of the terms to be selected. The equation (2.22) is equivalent in these co-ordinates to Laplace's equation $\nabla^2\rho = 0$ and is solved immediately by the introduction of an arbitrary distribution of matter $\sigma(x, y, z)$, of which ρ is to be the Newtonian potential.

If

$$R^2 \equiv (x - x')^2 + (y - y')^2 + (z - z')^2$$

then

$$\rho(x, y, z) = \frac{1}{4\pi}\int \frac{1}{R}\sigma(x', y', z')\, dx'\, dy'\, dz', \tag{2.31}$$

where the integral is taken throughout the (x', y', z') space.

The equations (2.23) are immediately integrable, and yield,

$$\left.\begin{aligned} \lambda+\rho &= g(z, x)+h'(x, y) \\ \mu+\rho &= f(y, z)+g'(z, x) \\ \nu+\rho &= h(x, y)+f'(y, z) \end{aligned}\right\}, \qquad (2.32')$$

where f, g, h, f', g', h' are arbitrary functions of the indicated variables, subject to conditions of differentiability and boundary conditions at infinity.

Since $\lambda+\rho=0$ when $y=\infty$, we must have $g(z, x)=-h'(x, \infty)$ so that g is a function of x only. Similarly, considering $z=\infty$, h' is a function of x only. Thus in virtue of the boundary conditions at infinity (2.32′) takes the form

$$\lambda+\rho=\mathrm{F}_1(x), \quad \mu+\rho=\mathrm{F}_2(y), \quad \nu+\rho=\mathrm{F}_3(z).$$

The arbitrary functions F_1, F_2, F_3 can be absorbed by a transformation of co-ordinates which does not affect their orthogonality, viz., using a function of the original x in place of x, etc. If x', y', z' are the new co-ordinates corresponding to x, y, z, the transformation takes the explicit form

$$x'=\int \tfrac{1}{2} e^{\mathrm{F}_1(x)}\, dx, \quad y'=\int \tfrac{1}{2} e^{\mathrm{F}_2(y)}\, dy, \qquad z'=\int \tfrac{1}{2} e^{\mathrm{F}_3(z)}\, dz,$$

the t co-ordinate remaining unaltered.

Hence without loss of generality we can take

$$\lambda+\rho=0 \ : \ \mu+\rho=0 \ : \ \nu+\rho=0.$$

§ 3. In view of the higher approximations it is convenient to carry out a change of notation. We substitute

$$p=\lambda+\rho, \quad q=\mu+\rho \ \text{ and } \ r=\nu+\rho,$$

so that p, q, r are of at least second order in $\sigma(x, y, z)$. Further instead of considering the Riemann contracted tensor $\mathrm{G}_{\mu\nu}$, we may work with independent linear combinations of $\mathrm{G}_{\mu\nu}$'s given by the material energy tensor-density $\mathfrak{T}_\nu^\mu$ where

$$\mathfrak{T}_\nu^\mu=\mathfrak{G}_\nu^\mu-\tfrac{1}{2}\delta_\nu^\mu \mathfrak{G}. \qquad (3.0)$$

Performing this change of notation we obtain after some calculation

$$\begin{aligned} 2\mathfrak{T}_1^1 = & -\tfrac{1}{2}(\rho_1^2-q_1 r_1) e^{\frac{1}{2}(-p+q+r)}+\tfrac{1}{2}(\rho_2^2-r_2 p_2) e^{\frac{1}{2}(p-q+r)} \\ & +\tfrac{1}{2}(\rho_3^2-p_3 q_3) e^{\frac{1}{2}(p+q-r)}+\frac{\partial}{\partial y}\{r_2 e^{\frac{1}{2}(p-q+r)}\}+\frac{\partial}{\partial z}\{q_3 e^{\frac{1}{2}(p+q-r)}\}, \quad (3.11) \end{aligned}$$

$$2\mathfrak{G}_4{}^4 = \frac{\partial}{\partial x}\{\rho_1 e^{\frac{1}{2}(-p+q+r)}\} + \frac{\partial}{\partial y}\{\rho_2 e^{\frac{1}{2}(p-q+r)}\} + \frac{\partial}{\partial z}\{\rho_3 e^{\frac{1}{2}(p+q-r)}\}, \qquad (3.12)$$

$$2\mathfrak{T}_1{}^2 = \{r_{12} + \tfrac{1}{2}(r_1 r_2 - r_1 p_2 - r_2 q_1 + 2\rho_1\rho_2)\} e^{\frac{1}{2}(p-q+r)}, \qquad (3.13)$$

together with $\mathfrak{T}_2{}^2$, $\mathfrak{T}_3{}^3$, $\mathfrak{T}_2{}^3$, $\mathfrak{T}_3{}^1$, which can be obtained by cyclic permutation of p, q, r and the suffixes 1, 2, 3 together.

The second order terms now yield,

$$\left.\begin{aligned} r_{22} + q_{33} + \tfrac{1}{2}(-\rho_1{}^2 + \rho_2{}^2 + \rho_3{}^2) &= 0 \\ p_{33} + r_{11} + \tfrac{1}{2}(\rho_1{}^2 - \rho_2{}^2 + \rho_3{}^2) &= 0 \\ q_{11} + p_{22} + \tfrac{1}{2}(\rho_1{}^2 + \rho_2{}^2 - \rho_3{}^2) &= 0 \end{aligned}\right\}, \qquad (3.21)$$

$$\rho_{11} + \rho_{22} + \rho_{33} = 0, \qquad (3.22)$$

$$\left.\begin{aligned} r_{12} + \rho_1\rho_2 &= 0 \\ p_{23} + \rho_2\rho_3 &= 0 \\ q_{31} + \rho_3\rho_1 &= 0 \end{aligned}\right\}. \qquad (3.23)$$

The equation (3.22) shows that ρ remains a potential function as far as the second order, and we may, if we wish, add a second order arbitrary function to $\sigma(x, y, z)$. This term may be used if desired to give some control over the second order terms of $\mathfrak{T}$, the invariant mass. We may choose by this means $\sigma(x, y, z)$ to be the distribution of material density present correct even to the second order. It can be shown that if this second auxiliary density is inserted the following general proof that all the seven gravitational equations can be satisfied by four functions λ, μ, ν, ρ can, with modification, still be demonstrated, but at present no purpose is served by its introduction and the second auxiliary density accordingly neglected.

The equations (3.23) may be immediately integrated, and in virtue of the fact that the perturbations are to vanish at infinity yield

$$p^{(2)} = -\iint_{yz}^{\infty} \rho_2\rho_3\, dy\, dz, \quad q^{(2)} = -\iint_{zx}^{\infty} \rho_3\rho_1\, dz\, dx, \quad r^{(2)} = -\iint_{xy}^{\infty} \rho_1\rho_2\, dx\, dy, \qquad (3.23$$

where, when necessary, the bracketed superscript denotes the order of the terms to be selected, and in the sequel when omitted will imply summation over the factors making up the appropriate weight.

It is necessary to prove that the solutions (3.23′) also satisfy the first three equations (3.21). This follows immediately thus,

$$\begin{aligned} r_{22}+q_{33} &= -\frac{\partial}{\partial y}\int_x^\infty \rho_1\rho_2\,dx-\frac{\partial}{\partial z}\int_x^\infty \rho_3\rho_1\,dx \\ &= -\int_x^\infty (\rho_{12}\rho_2+\rho_1\rho_{22}+\rho_{33}\rho_1+\rho_3\rho_{13})\,dx \\ &= -\int_x^\infty (\rho_{12}\rho_2+\rho_{13}\rho_3-\rho_{11}\rho_1)\,dx \\ &\qquad\qquad \text{in virtue of } \nabla^2\rho=0 \\ &= -\tfrac{1}{2}(-\rho_1^2+\rho_2^2+\rho_3^2), \end{aligned}$$

and similarly,

$$\begin{aligned} p_{33}+r_{11} &= -\tfrac{1}{2}(\rho_1^2-\rho_2^2+\rho_3^2) \\ q_{11}+p_{22} &= -\tfrac{1}{2}(\rho_1^2+\rho_2^2-\rho_3^2). \end{aligned}$$

Hence each of the equations (3.21) are satisfied, and we have found the complete solution correct to the second order. The explicit values correct to the second order are :—

$$\rho=\int_\tau \frac{1}{\mathrm{R}}\,\sigma(x',y',z')\,dx'\,dy'\,dz', \tag{3.31}$$

$$\lambda=-\rho-\iint_{yz}^{\infty}\rho_2\rho_3\,dy\,dz\,;\quad \mu=-\rho-\iint_{zx}^{\infty}\rho_3\rho_1\,dz\,dx\,;$$

$$\nu=-\rho-\iint_{xy}^{\infty}\rho_1\rho_2\,dx\,dy. \tag{3.32}$$

§ 4. Pursuing this process, we may produce a solution as far as any required order, the addition terms at each stage are determined by selecting the terms of successive orders from $\mathfrak{T}_1^2$, $\mathfrak{T}_2^3$, $\mathfrak{T}_3^1$, and $\mathfrak{G}_4^4$, and it can be shown that the remaining three equations $\mathfrak{T}_1^1=0$, $\mathfrak{T}_2^2=0$, $\mathfrak{T}_3^3=0$ are also satisfied.

If we select the terms of the nth order in σ from equations (3.12) and (3.13) we obtain :—

$$\nabla^2\rho^{(n)}=-\Sigma\frac{\partial}{\partial x}\left[\rho_1\left\{e^{\frac{1}{2}(-p+q+r)}-1\right\}\right], \tag{4.1}$$

and by integration

$$r^{(n)}=-\tfrac{1}{2}\iint_{xy}^{\infty}(r_1r_2-r_1p_2-r_2q_1-2\rho_1\rho_2)\,dx\,dy, \tag{4.21}$$

where Σ implies cyclical summation, and p, q are given by (4.2) after cyclical permutation of both p, q, r and suffixes 1, 2, 3.

The equation (4.1) immediately determines $\rho^{(n)}$, whose explicit value is

$$\rho^{(n)} = \frac{1}{4\pi}\int_\tau \frac{1}{\mathrm{R}}\Sigma \frac{\partial}{\partial x'}[\rho_1'\{e^{\frac{1}{2}(-p'+q'+r')} - 1\}]\,dx'\,dy'\,dz'. \tag{4.22}$$

It is found that the additional terms only occur at alternate stages, and are such that ρ possesses only odd orders of σ, whilst p, q, r may only have even orders. This follows immediately in general by induction from (4.1) and (4.22). Under these conditions it is found that $\mathfrak{T}_1^1$, $\mathfrak{T}_2^2$, and $\mathfrak{T}_3^3$ contain no odd terms so that for all odd orders of n they are identically satisfied. It remains therefore to give a general proof for even orders of n, that the solutions determined by (4.1) and (4.2) also automatically satisfy the equations (3.11).

We have

$$\begin{aligned}
2\mathfrak{T}_1^1 &= -\tfrac{1}{2}(\rho_1^2 - q_1r_1)\,e^{\frac{1}{2}(-p+q+r)} + \tfrac{1}{2}(\rho_2^2 - r_2p_2)\,e^{\frac{1}{2}(p-q+r)} \\
&\quad + \tfrac{1}{2}(\rho_3^2 - p_3q_3)\,e^{\frac{1}{2}(p+q-r)} + \frac{\partial}{\partial y}\{r_2e^{\frac{1}{2}(p-q+r)}\} + \frac{\partial}{\partial z}\{q_3e^{\frac{1}{2}(p+q-r)}\} \\
&= -\tfrac{1}{2}(\rho_1^2 - q_1r_1)\,e^{\frac{1}{2}(-p+q+r)} + \tfrac{1}{2}(\rho_2^2 - r_2p_2)\,e^{\frac{1}{2}(p-q+r)} \\
&\quad + \tfrac{1}{2}(\rho_3^2 - p_3q_3)\,e^{\frac{1}{2}(p+q-r)} + \tfrac{1}{2}\frac{\partial}{\partial y}\int_x^\infty (r_1p_2 + r_2p_1)\,e^{\frac{1}{2}(p-q+r)}\,dx \\
&\quad + \tfrac{1}{2}\frac{\partial}{\partial z}\int_x^\infty (q_1p_3 + q_3p_1)\,e^{\frac{1}{2}(p+q-r)}\,dx. \\
&\qquad - \frac{\partial}{\partial y}\int_x^\infty \rho_1\rho_2e^{\frac{1}{2}(p-q+r)}\,dx - \frac{\partial}{\partial z}\int_x^\infty \rho_1\rho_3e^{\frac{1}{2}(p+q-r)}\,dx,
\end{aligned} \tag{4.31}$$

since in virtue of (4.21), which is essentially an identity for all x, y, z,

$$\int_x^\infty (r_{12} + \tfrac{1}{2}r_1r_2 - r_1p_2 - r_2q_1 + 2\rho_1\rho_2)\,e^{\frac{1}{2}(p-q+r)}\,dx = 0,$$

and a similar equation in q.

Further

$$\int_x^\infty \rho_1\frac{\partial}{\partial x}\{\rho_1e^{\frac{1}{2}(-p+q+r)}\}\,dx = \rho_1^2e^{\frac{1}{2}(-p+q+r)} - \int_x^\infty \rho_1\rho_{11}e^{\frac{1}{2}(-p+q+r)}\,dx,$$

so that in virtue of (4.1),

$$\begin{aligned}
2\mathfrak{T}_1^1 &= \tfrac{1}{2}q_1r_1e^{\frac{1}{2}(-p+q+r)} - \tfrac{1}{2}r_2p_2e^{\frac{1}{2}(p-q+r)} - \tfrac{1}{2}p_3q_3e^{\frac{1}{2}(p+q-r)} \\
&\quad + \tfrac{1}{2}\frac{\partial}{\partial y}\int_x^\infty (r_1p_2 + r_2p_1)\,e^{\frac{1}{2}(p-q+r)}\,dx \\
&\quad + \tfrac{1}{2}\frac{\partial}{\partial z}\int_x^\infty (q_1p \;+ q_3\,p_1)\,e^{\frac{1}{2}(p+q-r)}\,dx \\
&\quad + \tfrac{1}{4}\int_x^\infty \Sigma\{\rho_1^2(-p_1 + q_1 + r_1)\,e^{\frac{1}{2}(-p+q+r)}\}\,dx.
\end{aligned} \tag{4.32}$$

Now in virtue of equations (3.11) up to the order $(n-2)$,

$$\tfrac{1}{4}\Sigma\int_x^\infty(\rho_1^2-q_1r_1)(-p_1+q_1+r_1)\,e^{\frac{1}{2}(-p+q+r)}\,dx$$
$$=-\tfrac{1}{2}\int_x^\infty p_1\frac{\partial}{\partial y}\{r_2\,e^{\frac{1}{2}(p-q+r)}\}+p_1\frac{\partial}{\partial z}\{q_3\,e^{\frac{1}{2}(p+q-r)}\}\,dx.$$

By making this substitution in the last term of (4.32) it is found that the total integrand is the partial differential with respect to x, of the first three terms occurring in (4.32), but has the opposite signs. Hence $\mathfrak{T}_1^1$ vanishes.

Similarly $\mathfrak{T}_2^2$ and $\mathfrak{T}_3^3$ vanish, and the solutions defined by (4.2) automatically satisfy the equations (3.11). Thus in spite of the orthogonality of the perturbed ground-form (1.0), under these conditions, a unique general solution exists, and is explicitly specified by equation (4.21) and (4.22).

§ 5. In virtue of the various restrictions which have been made, the foregoing analysis refers explicitly to a general statical distribution of matter. The equation (3.12) is, as was to be expected, Laplace's equation in terms of the perturbed co-ordinates. At any given stage in the approximation, the integral for ρ may be determined by expansion in any appropriate system of orthogonal functions, but we must beware that, by so doing, no special singularities are introduced. Alternatively it may be possible to eliminate such singularities by a method similar to that used by Prof. Weyl in a special case of axial symmetry, which involved laying down a definite restriction between the components of the material energy tensor.*

If the time co-ordinate is to be one of the explicit variables. We may make a transformation of the form,

$$x=it',\quad y=y',\quad z=z',\quad t=ix',$$

but the chief difficulty is the determination of the boundary condition as t becomes infinite. The Newtonian potentials will have to be replaced by retarded potentials, and under those conditions the arbitrary functions of the type f, f' (2.32) may be required. These functions, if required, are definitely determined by the boundary conditions, so that, in general, the solution remains unique, and no real difficulties are anticipated. It may happen, however, that an orthogonally perturbed ground-form will not suffice.

In the determination of the matter and stresses present, in the case when the system is periodic in t, the condition that the surfaces, over which $\mathfrak{T}_\nu^\mu$ is to be expressed as a boundary integral, must not cut the matter present, may be too stringent.

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* R. Bach, 'Math. Z.,' vol. 13, p. 142 (1922).

The Effect of Ozone on the Temperature of the Upper Atmosphere.—II.

By E. H. Gowan, D.Ph.

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Introduction.

A graphical method of calculating the radiative equilibrium temperature of the upper regions of the atmosphere, taking into account the variation of absorption with wave-length, has already been described in detail.* The equation of radiative equilibrium is most simply written in the form :

$$2\int_0^\infty K_\lambda B_{\lambda T_0}\, d\lambda = \int_0^\infty K_\lambda (S_\lambda + E_\lambda + A_\lambda)\, d\lambda,$$

where, for any arbitrary layer, K_λ is the absorption,† $B_{\lambda T_0}$ is the black body radiation at temperature T_0 degrees absolute, S_λ, E_λ, and A_λ are respectively the solar, terrestrial, and atmospheric radiations reaching the layer, all at wave-length λ. On account of the irregular variations of K_λ the integrations can only be performed graphically, and one cannot solve directly for the temperature. The term A_λ for any layer depends on the temperatures of all the other layers of the stratosphere, and unfortunately it is much too large to be neglected. Therefore it is evident that the process of determining the temperature distribution with height has to be one of successive approximation. On the basis of an assumed temperature distribution the terms of the equation are calculated. The total of the right-hand side then gives the energy that must be radiated by any layer. In general this is not equal to the radiation shown by the left-hand side for the assumed temperature. By calculating the left hand side for various other temperatures and plotting a curve, an estimate may be made of how near the agreement is. This serves as a guide in making a fresh assumption of the temperature distribution in order to start again. Such a process is continued until satisfactory agreement between assumed and calculated values is reached for all layers.

At the end of the first paper it was concluded that, given the layer of ozone, a theoretical consideration of an assumed condition of radiative equilibrium for water vapour and ozone, under solar and terrestrial radiation, indicates the existence of a warm region above 40 km. In this paper the work is carried much further, various changes in fundamental assumptions are tested, and the effects of some varying physical conditions are calculated.

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* 'Roy. Soc. Proc.,' A, vol. 120, p. 655 (1928).

† A glossary of terminology will be found at the end of the paper.

As before it has been assumed that the reflection of part of the solar energy takes place at, or effectively very near the tropopause, and that the resultant outgoing energy is capable of being absorbed in, and contributing energy to, the upper layers. The actual values given by Danjon* of the photographic and visible albedo, 0·56 and 0·29, have been used, the larger value for wavelengths shorter than 0·45 μ. The infra-red albedo is assumed zero, as in any case its effect was found to be quite negligible.

Experience has indicated the desirability of some modifications in the method of computation which result in a great saving of time and labour. Thus in practice a curve for E_λ was so constructed as to represent the radiation from the solid earth and the troposphere (instead, as previously, of taking it black at 260° absolute). The earth was assumed black at 280° absolute, and using, for about latitude 50° N., average temperature distribution with height, average relative humidity in the troposphere, and average cloud amount, the total outward radiation at 11 km. was calculated.† This average curve was then used in all subsequent computations, thus leaving A_λ to represent the total stratosphere radiation.

The most important change in practical detail has been the use of optical thickness as measured by water vapour, instead of the actual height difference, to specify the layers being considered. By this procedure one calculation of the absorption is sufficient for several approximations because one is considering a particular mass of gas for each layer, rather than that between two arbitrary heights. At the end of a series of approximations, when the temperature has been determined, it is possible to ascertain the heights. A considerable saving of time is thus effected. The only sacrifice involved is some loss of *initial* definiteness regarding the position of the ozone, particularly above its centre of gravity. The layers are chosen to represent certain heights with a given temperature distribution, and the position of the ozone associated with a specified amount of water vapour is approximately determined. At the end of a series of approximations, however, the temperature distribution is probably a different one, and thus the assigned height of the ozone may be somewhat changed. In view of the limited accuracy of the determinations of the effective height, and the fact that below 50 km. changes in temperature, and therefore in height, are relatively small, this was felt to be unimportant, and to be outweighed by the advantages.

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* ‘Ann. Obs. Strasbourg,’ vol. 2, p. 165 (1928).

† More consideration and comparison have resulted in the adoption of Hettner's absorption coefficients for water vapour. (‘Ann. Physik,’ vol. 55, p. 476 (1918).) They are more extensive, more detailed than Fowle's, and for a small amount of gas, not very different.

The former calculations were made assuming average conditions over the whole earth. For that purpose the solar energy was uniformly distributed over the surface. The results in this paper refer to midsummer at latitude 50° N., and the mean solar energy for these conditions has been used.

Results and Discussion.

It was pointed out in the previous paper* that, of the radiations considered in the equation of radiative equilibrium, only the solar is in a parallel beam. It was at first thought that radiation from terrestrial sources could be broken up into its horizontal and vertical components, whose equilibria, in a uniformly stratified medium, could be considered separately. It must, however, be recognised that rays through any layer of a medium traverse a shorter path if incident normally than if inclined at an angle. Hence the normal rays will suffer less absorption. Similarly the emission from any layer is the result of rays inclined at various angles, and the whole problem is rather complicated. There will be no difference between what one may call parallel and diffuse absorption in a layer if the absorption of a ray incident normally is complete. If the absorption of the normal ray is not complete through decrease in thickness of the layer, or decrease of absorption coefficient, the difference becomes increasingly appreciable.

The problem of taking the diffuseness accurately into account involves in general an increase in the absorption. Therefore the energies absorbed from E_λ and A_λ, and the radiation, are increased, but not the energy from S_λ. Thus the effect is not the same on both sides of the equation and cannot be cancelled out. Gold† has given a table of Exponential Integral Functions which can be used to obtain the absorption of any layer for diffuse radiation. It is also possible to use an approximation due to Schwarzschild,‡ which in practice means that the coefficient of absorption is multiplied by two, or that the path of an equivalent parallel beam makes an angle of 60° with the normal to the layer. The temperature distribution has been calculated using both these methods, and as the results were practically the same, they have been incorporated in a single curve. This is contrasted in fig. 1 with a curve for the same conditions using the absorption for a parallel beam.* When the absorptions are large the differences should be negligible; when small, perhaps considerable. It is therefore rather surprising that divergence begins only above 55 km. An explanation may be found in the fact that up to this height the absorbed energy due to E_λ and A_λ is a greater fraction of the total than that due to S_λ, in which case, of course, the correction tends to be equal on both sides of the equation. Above 55 km. the energy from S_λ is about 50 per cent. or more, and the increasing difference results.

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* pp. 658 and 667.

† 'Roy. Soc. Proc.,' A, vol. 82, p. 43 (1909).

‡ 'Gott. Nach.,' 1906, p. 41.

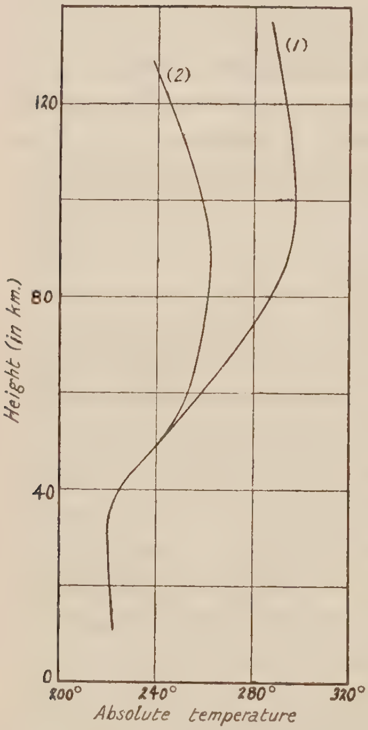

Fig. 1.—Effect of taking into account diffuseness of radiation. Ozone distribution B for 3 mm. Water vapour distribution A. Energy at midsummer, latitude 50°. Curve (1): all radiations considered as parallel beams. Curve (2): radiations from terrestrial sources diffuse.

From the fact that the high temperature in the upper stratosphere is maintained by the absorption of solar radiation one would conclude that a diurnal variation was, in the nature of things, probable. During the middle part of the day the radiation from the sun is above its mean value, and the layers which absorb short-wave solar energy will rise in temperature. During the hours of darkness these layers will be radiating more than they receive, since they are then only absorbing long wave terrestrial radiation. They must in consequence cool. But the height of any mass of gas which is in gravitational equilibrium (as the earth's atmosphere is on the average) depends on the temperature of the layers below it. It is obvious that the total amount of gas over any point does not change (except by horizontal flow) and that the thickness of a layer containing a given mass depends on its temperature.

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* Details of ozone and water vapour distribution are given in the glossary at the end of the paper.

Thus an increase in temperature of any layer pushes up by its expansion the layers above it, and conversely allows them to sink when it cools.

Preliminary estimates show that even small changes of temperature, say, 10 to 30 degrees, would produce appreciable changes in the heights of the upper layers from day to night. This drop of the upper layers consequent upon a reduced temperature below them will cause a horizontal pressure gradient over the boundary between the light and dark hemispheres. Some flow of air is bound to follow, and although the vertical component of the wind from light to dark may not be great, it is likely to be sufficient to prevent any marked settling out of the various constituents of the atmosphere according to their molecular weights.* The extreme case is that of complete mixing which will, since the partial pressure at the top of the troposphere is fixed, give much less water vapour in all the layers of the stratosphere than Dalton's law. They will radiate less, and since the absorption by ozone remains the same, their temperatures ought to be much higher. It is also worthy of note that flow of air from light to dark, that is from warm to cool, will tend to reduce any temperature change.

A great change in temperature during the night in summer has been calculated by Maris.† He has, however, taken no account of the variation of atmospheric radiation with temperature, and one or two important errors in his data have apparently crept in unawares. For example, Fabry is credited with the statement that the ozone layer is at 80 instead of 50 km. The CO_2 band at 14·7 μ is the correct width in Table IV, but approximately twice as wide in figs. 3, 4, and 5 which, one supposes, were used to obtain the integrated energies. For these and other reasons one is apt to regard the results doubtfully, but it is not the intention to criticise them in any detail here.

Independent evidence of circulation, and therefore mixing, in the layers at great heights in the atmosphere is, fortunately, available. Observations of persistent meteor trails‡ prove the existence of east winds between 30 and 80 km. and above that west winds, in the northern hemisphere. The velocities of luminous night clouds§ vary from 75 to 100 metres per second at heights between 27 and 83 km. The higher clouds travel generally from east to west, but some at about 27 km. have been observed to travel towards east-southeast. The green line in auroral displays* indicates the presence of oxygen up to 300 km. normally, and streamers occasionally reach 800 km. (when these layers are often still in sunlight). There is thus considerable evidence against the settling out of the heavier gases.

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* See glossary at the end of the paper.

† 'Terr. Mag.,' vol. 33, p. 233 (1928).

‡ Kahlke, 'Ann. Hydrogr.,' vol. 49, p. 294 (1921).

§ Quervain, 'Meteorol. Z.,' vol. 34, p. 132 (1917); Boll, *ibid.*, vol. 35, p. 316 (1918); Stormer, 'Geofys. Publ. Oslo,' vol. 5, nr. 2 (1927).

If there is sufficient convection to keep the constituents of the atmosphere completely mixed, or at least mixed up to heights far above 11 km., can a condition of radiative equilibrium exist ? It is evident that during the period of darkness an equilibrium would be characteristic of exchange of terrestrial radiations only. This gives very low temperatures in the upper layers, but even the most rapid cooling estimates indicate that such a condition is not reached during the night. The only relevant observations are those of meteors, and the densities calculated from them by Lindemann and Dobson† are such as would be due to a high temperature. The minimum in the frequency curve for heights of disappearance has been explained by supposing that when a meteor reaches a height of about 60 km. it passes more or less suddenly into colder air. This transition has the effect of momentarily checking the rate of evaporation from the surface, and a short interval elapses before the increasing density makes up the difference. Since disappearances indicate complete vapourisation there are very few in the neighbourhood of 55 km., and the secondary maximum occurs at about 45 km. All the meteor results given by Denning‡ have been analysed with respect to their time after sunset. They show only a slight filling up of this minimum during the course of the night, and its persistence indicates that there is no great drop in temperature above 60 km. They show also a small, rather doubtful, downward displacement of the maximum in the curve for heights of appearance. Any temperature effect on the latter maximum tends to be masked by a change in the relative velocity of the meteors. The rotation of the earth on its axis is in the same sense as its revolution round the sun. Hence during the early part of the night most visible meteors are following the earth and catching up on it, while later on they will be meeting it. The average relative velocity, therefore, tends to increase during the night. This counteracts the effect of a drop in temperature, since fast meteors appear higher up than slow ones, other things being equal. Thus the evidence from meteors is against any large diurnal temperature change, but it offers no proof that a small one is impossible.

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* Bartels, ‘Ergeb. d. Exact. Naturwiss.,’ vol. 7, p. 120 (1928), where a bibliography is given.

† ‘Roy. Soc. Proc.,’ A, vol. 102, p. 411 (1922).

‡ ‘M. N. R. Astr. Soc.,’ vol. 57, p. 161 (1897); vol. 72, p. 423 (1912); vol. 76, p. 219 (1916).

From the considerations enumerated above it appears very probable that the temperature and height oscillations are appreciable but small enough for a mean radiative equilibrium to hold. A certain amount of convection is even possible without much disturbance of the condition of strict radiative equilibrium. Suppose the net radiation from or to unit mass of gas is R calories per minute if it differs in temperature 1° from its surroundings. Then its rate of change of temperature with time is R/S degrees per minute if S is the specific heat. For adiabatic rise or fall in the atmosphere 1° = 100 metres. Hence any mass of air can rise or fall R/S × 100 metres per minute without departing more than 1° from its equilibrium temperature. The following table gives the approximate allowable velocities at various heights if the temperatures are to remain within 1° of their equilibrium values, net radiations being calculated for water vapour distribution B.

Height	15	32	43	54	66	80	105	140	km.
Velocity ..	0·01	0·05	0·13	0·26	0·36	0·42	0·51	0·77	km./day.

These small velocities which will ensure ample mixing up to very great heights, will not appreciably affect a radiative distribution of temperature.

From the fact that the allowable velocity in the above table increases with height it is clear that so also does the rate of exchange of energy by radiation, since this is the governing factor. Equilibrium is therefore more likely in the upper layers than in the lower. But it is known that a convective gradient does not persist into the stratosphere, and it follows that even in the lower layers the temperature gradient is governed by radiation, not by convection. Thus it seems safe to assume that throughout the stratosphere the temperature conditions are determined by radiation, and not by any convection that may exist. There follow further calculations based on the assumption of a condition of mean radiative equilibrium through 24 hours.

Fig. 2 contrasts and compares the effects of various changes in the assumptions regarding the distributions of water vapour and ozone. In computing these curves the temperatures are regarded as possible, *i.e.*, the increased thermal decomposition of the ozone is not taken into account. Curves (1), (2), and (4) show what an enormous difference in the temperatures and temperature gradient results from assuming mixing to continue much higher than 11 km. Curves (3) and (5) show how the temperature falls off again above 80 or 100 km. if the ozone is taken at its minimum distribution A, *i.e.*, proportional to the oxygen above its centre of gravity.

The amount of energy in the solar ultra-violet spectrum has a crucial bearing on all the work in this and the previous paper. The data used throughout were given by Fabry and Buisson,* and depend on their assumption that the positive crater of the carbon arc radiates as a black body. While this is probably not far from the truth, it may introduce an appreciable error, and in any case the values beyond 2900 A. are extrapolation, since no energy of shorter wave-lengths than this gets through the ozone to be observed at the surface of the earth. It is also possible that there are undetectable Fraunhofer lines in the region covered by the ultra-violet ozone band. For any or all of

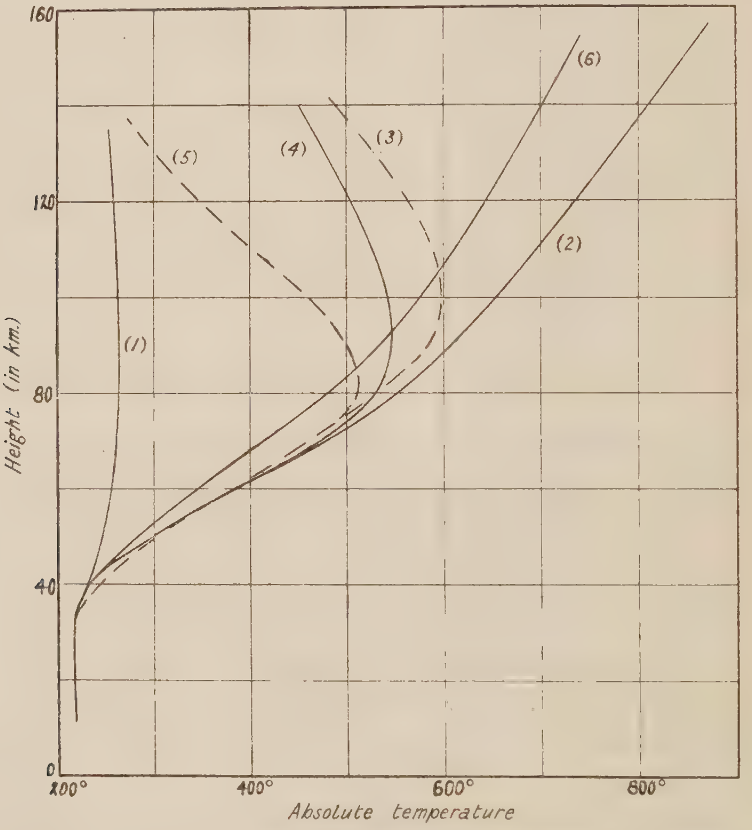

Fig. 2.—Effect of various assumptions regarding distribution of water vapour and ozone. Curve (1): ozone distribution B, water vapour A. Curve (2): ozone distribution B, water vapour B. Curve (3): ozone distribution A, water vapour B. Curve (4): ozone distribution B, water vapour C. Curve (5): ozone distribution A, water vapour C. Curve (6): similar to (2) but with one-half so much solar energy.

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* 'C. R.,' vol. 175, p. 156 (1922).

these reasons the solar energy used may have been too great, and smaller energy naturally means lower temperatures. An idea of the magnitude of the effect may be obtained from fig. 2, where curve (6) differs from curve (2) only in having one-half so much solar energy available in the ultra-violet. It is perhaps unlikely that any discrepancy could be greater than this, but it must be recognised that to consider the solar radiation as " black " at 6000° absolute beyond 2900 A. is a fundamental assumption for this work.

The question of how high it is physically possible for the temperature of the ozone layer to be maintained is important in this connection. The three factors operating to produce a combined temperature and concentration equilibrium at any height are : the formation of ozone by the absorption of solar energy in the short ultra-violet and by some other agency from outside the earth ; the absorption by the ozone of longer wave solar radiation producing the high temperature ; and the ordinary decomposition due to the temperature. (The absorption of radiant energy by ozone may produce some photochemical decomposition, but it is not unlikely that this is really due to the thermal effect of the high temperature resulting from the absorption.) Since increase in temperature accelerates the decomposition, an upper limit to the temperature is set by the rate of decomposition combined with the rate of formation, assuming the latter to be independent of temperature. Under equilibrium conditions the heat of the chemical reaction has no effect.

The reaction $2O_3 = 3O_2$ is of the type known as bimolecular, *i.e.*, the rate of decomposition of ozone is proportional to the square of its concentration.* If a is the initial concentration (fractional) and that after time t is $(a - x)$, then $\frac{dx}{dt} = k(a - x)^2$ for constant temperature. Therefore $kt = \frac{x}{a(a - x)}$. Call τ the time for the concentration to fall to half its initial value. Then $\tau = \frac{1}{ka}$, where k is known as the velocity constant and is a function of the temperature. Arrhenius found empirically that the variation of k can be expressed satisfactorily by the equation :

$$\frac{d \log k}{dT} = \frac{A}{RT^2} \quad \text{or} \quad \log k = C - \frac{A}{RT}.$$

R is the gas constant expressed in calories per gram-molecule, A and C are constants depending on the kind of gas and possibly on other factors. T is the absolute temperature. Thus the logarithm of the velocity constant plotted against the reciprocal of the absolute temperature gives a straight line, and this takes into account any part of the reverse reaction, $3O_2 = 2O_3$, which may be due to temperature alone.

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* See Hinshelwood, " The Kinetics of Chemical Change in Gaseous Systems," p. 41.

Taking 3 mm. of ozone as the total amount present, the approximate concentrations in the various layers being considered were determined. Using a combination of the data given by Hinshelwood,* and by Wulf and Tolman,† fig. 3 has been prepared. The half life periods were calculated for the layer of maximum concentration over a suitable range of temperature neglecting the rate of formation of ozone in the atmosphere. Then holding τ constant the corresponding temperatures for the other layers were found, and the family

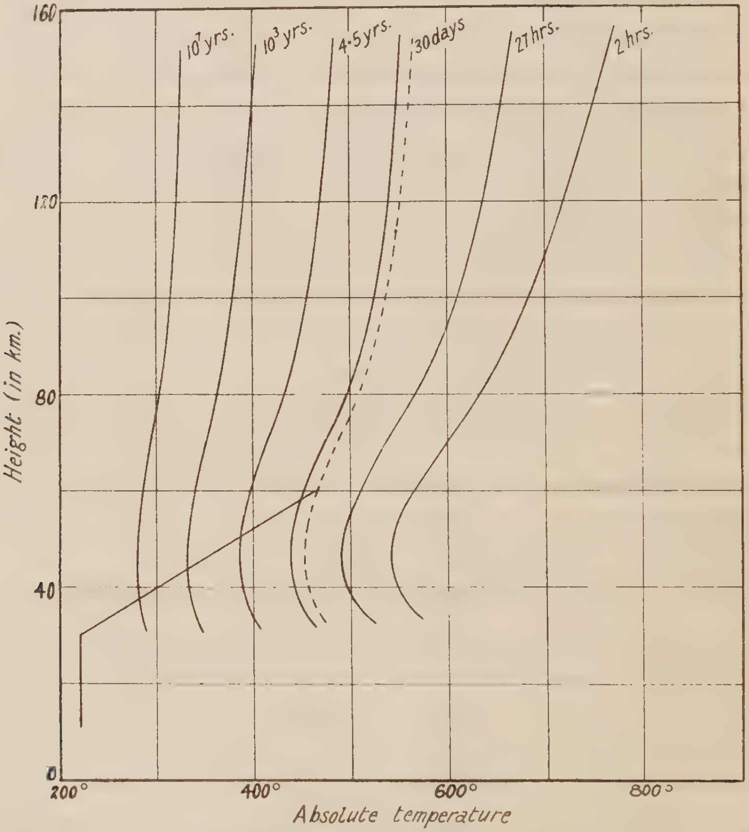

Fig. 3.—Thermal decomposition of atmospheric ozone. Distribution B for 3 mm. of ozone. A family of curves showing the variation of temperature with height for several given values of the half-life period, τ. Dotted curve shows maximum temperature for observed rate of change of ozone.

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* *Loc. cit.*, p. 61.

† 'J. Am. Chem. Soc.,' vol. 49, p. 1650 (1927).

of curves plotted. An extrapolation for k is involved but it is linear, and all other indications point to its being legitimate. Each curve then shows the possible temperature at various heights if the rate of formation of ozone is rapid enough to cope with the rate of decomposition represented by the appended value of τ, which is the half-life if no fresh ozone is being formed and the temperature remains constant. It is therefore only of use for purposes of comparison, since there must be a certain amount of cooling after sunset. There is as yet no sure evidence of a diurnal variation in the amount of ozone, the values at morning and evening being the same. The first measurements made at night showed an increase over the day, but more certain values are highly desirable, since any cooling should allow the accumulation of more ozone. This seems to happen during the polar night, maximum ozone being observed in high latitudes in spring, whereas low latitude stations show a relatively small amount which is very nearly constant during the year. These observations indicate that the solar ultra-violet light is not the only agency of ozone formation in the upper atmosphere. There is probably an unknown one of equal importance which can operate over the dark hemisphere. The temperatures represented by the curves, then, apply to a concentration and temperature equilibrium averaged over 24 hours.

The measurements of Dobson and his co-workers* show changes in ozone up to 1 mm. occurring in times of the order of a day, but these seem possibly to be due to actual change of air. Low latitude stations have, at times, had a sudden rise in the amount of ozone. The values then slowly drop back to normal at the rate of 1 to 2 per cent. per day, or about 50 per cent. per month. This is probably near the normal rate of thermal decomposition, though there may also be the small photo-chemical effect. Thinking merely of orders of magnitude and knowing the approximate initial concentrations, this rate gives an independent indication of the temperature of the ozone layer, and the broken curve in fig. 3 shows the indicated upper limit.

Now that the origin of the green line in the auroral spectrum has been determined, Babcock's† measurement of the line width enables the temperature at auroral heights to be estimated. Fabry and Buisson‡ have worked out from the Doppler effect the following expression for the width of a line:

$$\Delta = 0\cdot 82 \times 10^{-6} \lambda \sqrt{\frac{T}{M}},$$

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* 'Roy. Soc. Proc.,' A, vol. 110, p. 660 (1926); vol. 114, p. 521 (1927); vol. 122, p. 456 (1929).

† 'Astrophys. J.,' vol. 57, p. 209 (1923).

‡ 'J. de Phys.,' 5 série, vol. 9, p. 189 (1919)

where Δ = width of line ; λ = wave-length in Angstrom units ; T = absolute temperature, and M = atomic weight of emitting molecule. The wave-length is 5577 Ångströms, and the width given is 0·035 Ångströms. Taking the atomic weight to be 16, as usual, one obtains for the temperature a value of about 900° absolute. This refers to heights above 100 km. and is a maximum since the whole width of the line is attributed to the Doppler effect. The estimate is therefore a useful confirmation of the possibility of temperatures of that, or a somewhat lower order, existing there.

The actual values of all the absorption coefficients used in this work are of great importance. In the previous paper it was pointed out that those of water vapour in the infra-red varied in the same sense as the total pressure. An international conference was held in Paris from May 15 to 17, 1929, to discuss problems connected with ozone and general atmospheric absorption. There A. Ångström claimed that as the pressure approaches zero the absorption in the infra-red of a given mass of water vapour approaches a limit which is not very different from zero. The details of the experiments on which the claim is based were not given, but Ångström inferred from them that all the energy absorbed by atmospheric ozone in the ultra-violet must be radiated by it alone in the infra-red. If molecules do not spontaneously re-emit absorbed energy they must hold it till a collision, perhaps of a particular kind, occurs, and while they are still in possession of their quantum, can absorb no more. It would then be quite conceivable that with lowered pressure and fewer collisions a state similar to saturation is set up, thus lowering the absorption coefficient. If this were the case a variation of absorption with incident energy would also be expected, since if it were small enough the saturation state could not be reached.

The coefficients of absorption for ozone in the infra-red were taken from the data given by Ladenburg and Lehmann.* They are apparently much smaller than the values found by K. Ångström† in the laboratory, and also by identifying and measuring absorption bands in the solar spectrum. This discrepancy cannot be explained by such a pressure effect as that in the preceding paragraph since it is in the opposite direction. For the sake of completeness the effect on temperature calculations of using the infra-red coefficients given by K. Ångström for ozone is illustrated in fig. 4, full notes on the conditions governing the calculation of each curve being given.

The amount of ozone in the atmosphere varies with the type of weather, the time of year, and the latitude. It is thus to be expected that some change in the temperature of the upper stratosphere would result, and calculations

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* 'Ann. Physik,' vol. 21, p. 305 (1906).

† 'Arkiv. Matem. Astrom. Fysik,' vol. 1, pp. 347, 396 (1904).

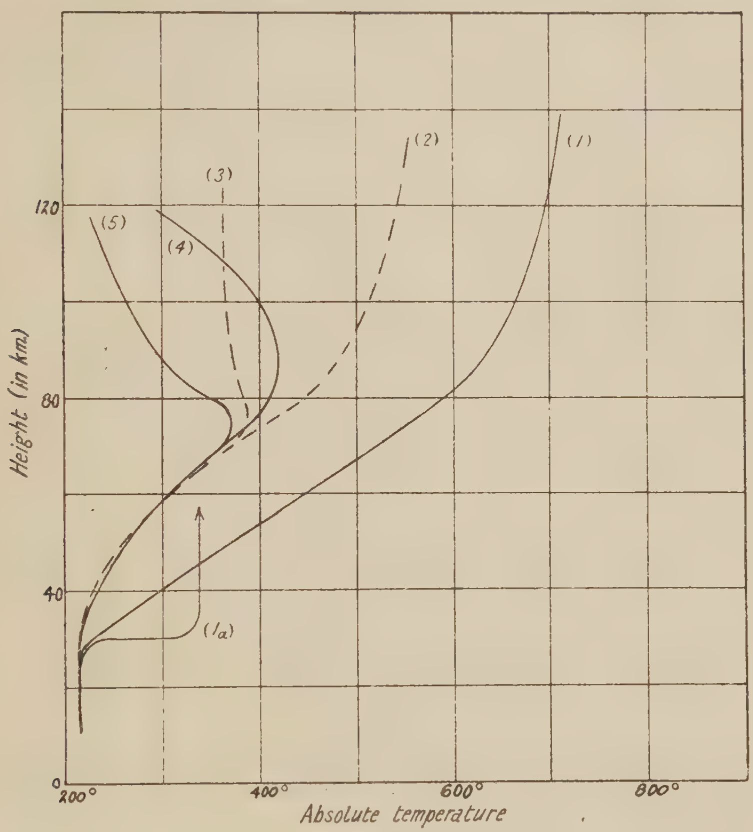

Fig. 4.—Effect of using Ångström's value of the ozone absorption coefficient in the infra-red. Curve (1): ozone distribution B, water vapour inactive above about 30 km., or below total pressure of about 2 mm. Curve (1) *a*: the whole of the ozone treated as a unit above 30 km., water vapour inactive. Curve (2): ozone distribution B, water vapour B. Curve (3): ozone distribution B, water vapour C. Curve (4): ozone distribution A, water vapour B. Curve (5): ozone distribution A, water vapour C.

have been made using 2 and 4 mm. of ozone, as well as the 3 mm. which has been taken as the average. Fig. 5 compares the magnitude of the effect with the two distributions of water vapour. In each case the temperature changes are relatively small.

If the sun is not at, or very near the zenith, the effective thickness of absorbing material is greater, and so also is the area over which the energy is spread.

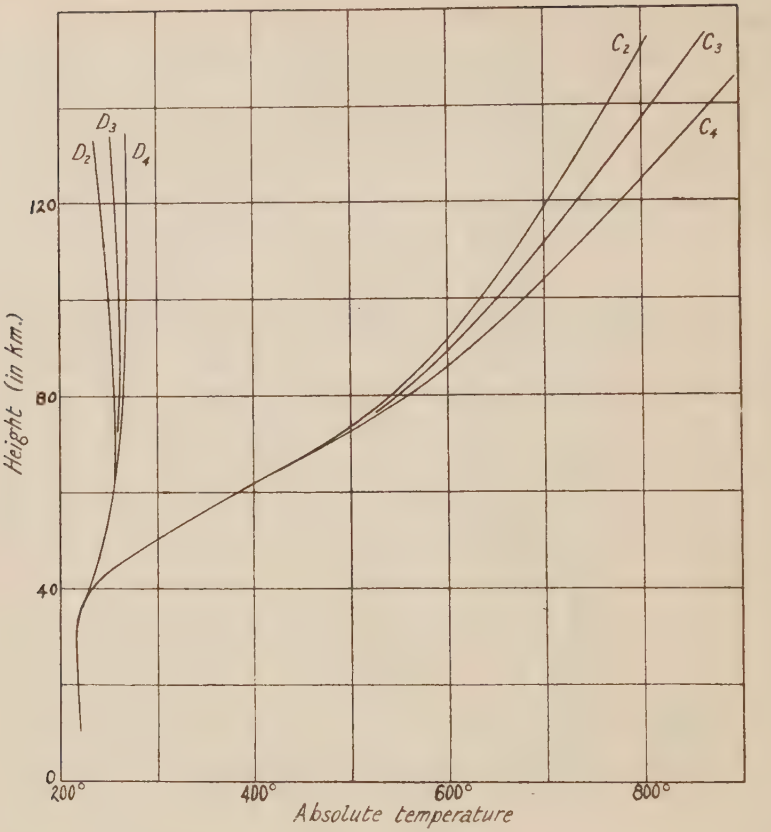

Fig. 5.—Effect of variations in amount of ozone, distribution B. D-family : water vapour distribution A. C-family : water vapour distribution B. Subscripts 2, 3, 4, represent total amount of ozone, millimetres.

Suppose the energy in the solar beam is E per unit normal area, and the zenith angle is Z. The energy absorbed in a layer of vertical thickness x, after the original beam has passed through a vertical thickness x_1, is :

$$\mathrm{E}\cos \mathrm{Z}\,.\,10^{-ax_1 \sec \mathrm{Z}}\,(1 - 10^{-ax \sec \mathrm{Z}}).$$

Thus for a lower altitude of the sun more energy tends to be concentrated in the upper layers. Near the top there will be a certain amount of compensation between increased energy and increased area, and the resulting temperature differences will tend to be smaller than lower down where there is no such compensation.

By considering 3 and 4 mm. as different effective thicknesses of 2 mm. of ozone measured vertically, they correspond to angles of 48° and 60° respectively. Hence a short calculation for these zenith angles is possible by proper treatment of the absorbed solar energies obtained in the course of preparing fig. 5. This has been done using two distributions of water vapour, with the result shown in fig. 6. These curves may be taken to represent the effect of change of latitude for a given season, or change of season for a given latitude, and give some idea of the relative magnitudes.

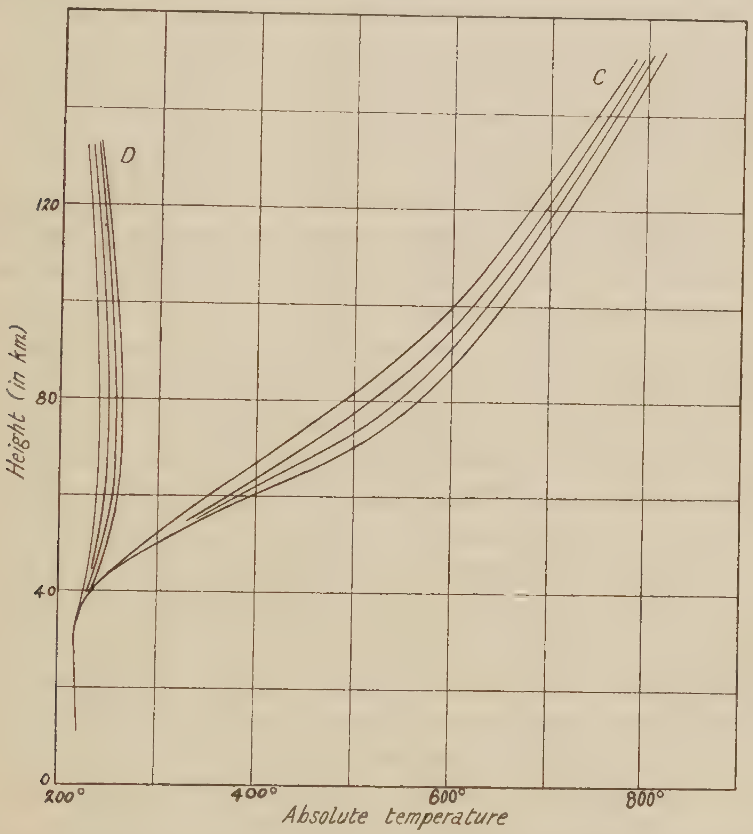

FIG. 6.—Effect of zenith angle of sun. Ozone distribution B for 2 mm. total. D-family: water vapour distribution A. C-family: water vapour distribution B. From right to left the curves are for zenith angles of 0, 28, 48 and 60 degrees.

A suggested variation of absorption coefficient with the total pressure has already been mentioned.* If this phenomenon is general in the infra-red, one cannot consider the coefficient constant and use it to calculate the absorption of various layers at widely differing pressures. Higher temperatures result from decreased long-wave absorption and radiation. Though this variation may not be confined to the infra-red, but may be operative also in the visible and ultra-violet, the energy absorbed there will be unchanged. It is the coefficient of absorption in the atmosphere that is actually measured, and the amount of ozone is deduced by comparison with laboratory experiments. The amount may be wrong therefore, but the relative changes will be right. While any variation in the short-wave region is, in fact, fundamental for all measurements of the absolute amount of ozone in the atmosphere, it will have no effect on the calculation of the energy absorbed and hence none on the temperature.

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* Several of those present at the Paris Conference signified their intention of submitting the matter to careful investigation.

Another factor having a similar effect is that of the purity of the spectrum. If the resolution is incomplete it is impossible to calculate from one thickness of gas the absorption due to a different one, since Beer's law does not hold for the average over a series of fine absorption lines. This has been carefully investigated for the ultra-violet ozone band which is used in measuring the quantity of ozone in the atmosphere,* and no fine structure was detected there. The matter has not been settled with such certainty in the infra-red for water vapour and ozone, and some doubt as to the applicability of the law in this region remains. The use of it in this paper is only justified by the fact that no other law is available, and empirical results give no guidance. In practically every case a calculation from large to small amount of absorbing material is involved, and the resulting values of the absorption are therefore too small. If this correction, in the long wave region, could be applied, it would increase the radiated more than the absorbed energy, and lower the values of the temperature. There might be some justification for the claim that the pressure and spectral purity corrections to the long wave absorption tend to cancel each other, but the degree of compensation is impossible to estimate.

It has been assumed that all the energy absorbed in the ultra-violet is re-radiated in the infra-red. However, the probability of a molecule having time to re-emit some sort of fluorescent radiation increases with the mean free path, and this might become important at great heights. Hartley† found a marked fluorescence in ozone through glass, but Rayleigh‡ could detect none even through quartz, using a quartz mercury lamp as the source of the exciting radiation. It is thus most improbable that fluorescence could be appreciable at low pressures.

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* Lauchli, A., 'Z. Physik,' vol. 53, p. 92 (1929).

† 'Nature,' vol. 39, p. 474 (1889).

‡ 'Roy. Soc. Proc.,' A, vol. 100, p. 376 (1922).

By means of a specially constructed furnace, and exposures of from 24 to 150 hours, Stuchtey* analysed the light from rapidly decomposing ozone at 350 to 400° C. and atmospheric pressure. He found emission bands corresponding with all the well-known absorption bands in the visible and ultra-violet. The intensity was not measured, but the exposures required indicate that the lines were very weak, and it was, in fact, stated that the plates were not suitable for reproduction. A very small fraction of the molecules of the decomposing gas, then, give out energy in short wave-lengths, and even making a generous allowance for increase in that fraction at low pressures, practically all the absorbed energy will be transformed into heat. It seems that no other assumption would be nearer the truth, and certainly could not be more useful, than the one tacitly made at the beginning of this work.

Consideration of the spherical shape of the earth brings in the fact that for the same solid angle an area of 1 sq. cm. at the surface is just less than 1·05 sq. cm. at a height of 150 km. E_λ and A_λ do not, therefore, pass through exactly the same area in each layer, but in view of other uncertainties in the data, the correction is not worth making. Similarly the solar energy has not been corrected, as the value of the constant used was obtained by taking the mean distance of the earth from the sun. There would be no correction to the radiation from a layer. When the effect of the area increasing upwards became appreciable, it would give slightly lower temperatures.

During the course of the calculations it was possible to obtain values of the total outward radiation at latitude 50° N. embodying all the assumptions used, and with the calculated temperatures in the stratosphere. For midsummer, with water vapour according to Dalton's law the value is 0·278, with water vapour according to complete mixing, 0·287 cal./cm.^{2} min. The average amount of energy to be got rid of by the earth is $\frac{1}{4}\, 1{\cdot}953 \times 0{\cdot}57 = 0{\cdot}28$ cal./cm.^{2} min., using the albedo given by Aldrich† for a mean cloud amount of 0·52, viz., 0·43. For intensity of outgoing terrestrial radiation at 50° N. latitude in July Simpson‡ gives 0·284 cal./cm.^{2} min. The good agreement among these figures is most satisfying and serves as a useful check. It is also a justification of the assumptions and method of calculation. It may be remarked as a further important justification that in every case the temperature obtained for the layer from about 11 to 30 km. agrees very well with the values known from registering balloon ascents.

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* 'Z. Wiss. Photographie,' vol. 19, p. 161 (1920).

† Smithsonian Inst., 'Ann. Astr. Obs.,' vol. 2, p. 162 (1908); 'Misc. Coll.,' vol. 69, No. 10, p. 8 (1919).

‡ 'Mem. Roy. Met. Soc.,' vol. 3, p. 75 (1929).

Conclusions.

Both sound wave and meteor phenomena can be satisfactorily explained by this high temperature in the upper stratosphere. The return of low frequency sound waves from heights of about 40 km. requires the temperature to be nearly 300° absolute there. From registering balloon records it is known that the temperature is not very different from 220° absolute in temperate latitudes between 11 and 25 or 30 km. Hence the rate of increase in temperature from 30 to 40 km. must be something more than 6° per kilometre.

In the curves for heights of disappearance of meteors the minimum at 55 km. is surprisingly distinct, since errors in observation tend to smooth it out. The only explanation of its existence so far put forward is a sharp drop in temperature about 60 km., which momentarily reduces the rate of evaporation from the meteor. Thus it seems that the temperature continues to rise from 30 to at least 60 km. A change from 300° to 220° between these heights is inadequate to give a sufficient drop in the rate of evaporation except for slow meteors. Using temperatures such as are obtained in this paper the drop would be much greater, and the explanation would then fit quantitatively as well as qualitatively, and for average meteors.

A uniform gradient from 30 to 60 km. of more than 6° per kilometre would lead to a temperature of over 500° absolute at the latter height. Temperatures of this order have been shown to be quite possible of attainment and maintenance under some of the assumptions made.. The densities calculated from such a high temperature agree remarkably well with those calculated by Lindemann and Dobson from meteors,* whereas those authors merely claimed that the temperature was higher than was generally supposed, and suggested the order of 300°. This lower temperature, however, is insufficient to obtain agreement between ordinary calculations of density and those from meteors.†

From observational evidence and the various calculations completed in this paper, then, it may reasonably be concluded: that the constituents of the atmosphere are mixed far above 11 km. (except ozone, which is continually being formed and destroyed at certain great heights); that a probable distribution of ozone and water vapour can maintain a temperature of over 500° absolute from 60 km. upwards; and that the temperature gradient from 30 to 60 km. is approximately the reverse of its value from the ground to the tropopause.

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* *Loc. cit.* Their theory has been adversely criticised by Sparrow ('Astrophys. J.,' vol. 63, p. 90 (1926)), but Lindemann's reply deals successfully with the points raised ('Astrophy. J.,' vol. 65, p. 117 (1927)).

† *Cf.* Whipple, 'Nature,' vol. 118, p. 312 (1926).

In fig. 3 is drawn a curve fulfilling these conditions up to 60 km., near which point it intersects the dotted curve described above. There may then be some justification for the claim that this paper supplies an adequate explanation of both sound wave and meteor phenomena. That the three lines of work should agree more closely than to the same order of magnitude is hardly to be expected in their present stage of accuracy and development.

Summary.

The previously described method is made more tractable by some simplifications, and the diffuseness of radiations from terrestrial sources is taken into account. Preliminary estimates of the rate of cooling of the upper layers of the stratosphere, and consideration of independent observational evidence lead to the belief that mixing of the constituents is general far above the tropopause. The radiation from the stratosphere must then be less, and since the absorption of solar energy is the same, higher temperatures result. The question of the maximum temperature attainable is examined, it being governed by the rate of thermal decomposition of ozone, and the rate at which ozone is formed in the atmosphere. The assumption of radiative equilibrium is re-examined in the light of the occurrence of sufficient convection to ensure mixing, but is retained. The effect of the two distributions of water vapour is illustrated by calculations for various conditions, as are also the effects of different distributions and amounts of ozone, and different zenith angles of the sun. It is concluded that plausible distributions of ozone and water vapour provide the basis for a quantitative explanation of sound wave and meteor phenomena.

Glossary of Terminology.

Coefficient of Absorption.—Suppose a parallel beam of radiation, whose intensity is I_0 passes through a thickness of gas x, and on emerging the intensity is I. Then $I = I_0\, 10^{-\alpha x}$, where α is the coefficient of absorption. For ozone x is measured in centimetres of the pure gas at N.T.P.; for water-vapour it is the thickness in centimetres of the layer of water which would result if the vapour were all condensed.

Absorption.—This is the ratio of the energy absorbed to the incident energy, and is therefore $(I_0 - I)/I_0 = 1 - 10^{-\alpha x}$.

Ozone Distribution A.—Measurements of the height of the centre of gravity, or effective height of the ozone layer indicate that it is between 40 and 50 km. above the surface of the earth. Beyond this height the most plausible supposition is that the ozone cannot be less than proportional to the oxygen. It is assumed that below the layer of maximum concentration the amount of ozone falls off much more rapidly than above it, and the layers from 30 to 40, and from 50 to 60 km. approximately, are assigned the same amounts. Below 30 km. it is assumed there is none.

Ozone Distribution B.—Whatever the ozone forming agency may be it is certainly extra-terrestrial. Therefore it is very likely that there is more ozone in the top layers than would be proportional to the oxygen, since the agency will be weakened as it penetrates the atmosphere. In the previous paper a trial redistribution was made to see what change would be necessary to keep the temperature approximately constant above 60 km. That involved increasing the ozone in the top four layers by factors of 10·3, 2·1, 1·1, and 1·05 respectively, starting with the top. The ozone in the layer of maximum concentration was decreased by a factor sufficient to keep the total amount the same, and the other layers were left unchanged. This distribution is here used, and called B.

Water Vapour Distribution A.—If in the stratosphere there is no convection the individual gases are, at all heights, in gravitational equilibrium with their own partial pressures. This is known as Dalton's law, and under it the proportion of the lighter gases increases with height. In particular this law gives the largest possible amounts of water vapour in the stratosphere, equal to the weight supported by the partial pressure at the tropopause, 11 km. This pressure has been taken throughout as that corresponding to saturation at 219° A.

Water Vapour Distribution B.—If there is sufficient convection throughout the stratosphere to maintain constant composition the water vapour is in a fixed proportion to the total pressure, above 11 km.

Water Vapour Distribution C.—An assumption of constant composition as in B up to about 70 km., and above that distribution according to Dalton's law as in A.

Acknowledgments.

I wish to take this opportunity of gratefully acknowledging grants from the Meteorological Office and the Rhodes Trust, through whose support the continuation of these calculations was made possible. I desire also to thank Prof. F. A. Lindemann, Dr. G. C. Simpson, and Dr. G. M. B. Dobson for valuable advice and suggestions during the course of the work.

The Density and Compressibility of Phosphine Gas; the Atomic Weight of Phosphorus.

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(Communicated by Sir James Walker, F.R.S.—Received February 11, 1930.)

Phosphorus is an element of which the recognized atomic weight is subject to some uncertainty. The last Report on Atomic Weights issued by the Chemical Society* adopts the Aston† value of 30·98 (2), based on results obtained by the mass-spectrograph; but the Reports of the German and the American Commissions on Atomic Weights‡ show adherence to the older and higher value of 31·02, derived mainly from chemical analysis.§ These values differ by more than 0·1 per cent.

In addition to the above methods of atomic-weight determination, there is the method depending on the determination of the normal density and compressibility of some gaseous compound of the element concerned. The present investigation is an attempt to determine the normal density and compressibility of phosphine gas. The compressibility coefficient is not a small one, but the gas is suitable in that it contains only a small proportion of the lightest element, hydrogen, in its composition; the error involved in deriving the atomic weight of phosphorus from the molar weight of phosphine is thus negligible. The published values, however, for both density and compressibility are few in number and not concordant.

Pickering, in the "International Critical Tables,"|| gives the normal density of phosphine as 1·5294, this figure being based on the value 1·5293 given by G. Ter Gazarian¶ and by M. Bretschger.** This value is also cited in the Landolt-Börnstein Tabellen. Earlier values are noticeably discordant, 1·52058 being

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* 'Trans. Chem. Soc.,' p. 218 (1929).

† 'Roy. Soc. Proc.,' A, vol. 115, p. 487 (1927).

‡ 'Ber. D. Chem. Ges.,' vol. 63, p. 1 (1930); 'J. Amer. Chem. Soc.,' vol. 52, p. 861 (1930).

§ *Cf.* Baxter and Jones, "Analysis of Silver Phosphate," 'J. Amer. Chem. Soc.,' vol. 32, p. 298 (1910); Baxter, Moore and Boylston, "Analysis of Phosphorus Trichloride," vol. 34, p. 259 (1912); Baxter and Moore, "Analysis of Phosphorus Tribromide," vol. 24, p. 1637 (1912).

|| Vol. 3, p. 3 (1928).

¶ 'J. Chim. Phys.,' vol. 7, p. 337 (1909).

** *Cf.* Mellor's "Inorganic and Theoretical Chemistry," vol. 8, pp. 807 and 820.

given in Abegg's "Handbuch" (1907) and 1·5315 by Berthelot (1898),[*] based on experiments by Leduc.[†]

The available figures representing compressibility show a similar variation. Direct measurements are few in number. Gazarian gives

$$A_0^1 = A_1^2/(1 + 4A_1^2) = 0\cdot00828,$$

where A_1^2 is derived from direct measurements of Leduc, and is defined by the usual equation

$$1 - (p_2v_2)/(p_1v_1) = A_{p1}^{p2}\,(p_2 - p_1).$$

Taking $(pv)_0/(pv)_1 = 1 + \lambda$, in the usual notation, $1 + \lambda = 1\cdot0084$. Other values given by Gazarian, based on critical data by Leduc and Sacerdote and by Briner, are :—

$$A_0^1 = 0\cdot00939 \text{ (L. and S.), whence } 1 + \lambda = 1\cdot0094$$

and

$$A_0^1 = 0\cdot00967 \text{ (B.), whence } 1 + \lambda = 1\cdot0098.$$

Berthelot (*loc. cit.*) gives $A_0^1 = 0\cdot00937$ (also based on Leduc's values for T_c and P_c), whence $1 + \lambda = 1\cdot0095$.

The value for the atomic weight of phosphorus obtained by Gazarian is 30·92. The compressibility figures are admittedly uncertain and the final value for the atomic weight appears definitely to be too low.

The method employed in this investigation is the common indirect method of finding the density under pressures varying from one atmosphere to as near zero pressure as is consistent with accuracy. If a certain weight W of gas occupies a volume v under pressure p, then the density "per unit pressure"[‡] is equal to W/pv. For a perfect gas W/pv would be independent of the pressure, since the product pv would then be constant ; for an actual gas such as phosphine the values obtained for the density "per unit pressure" are inversely proportional to pv and can therefore be conveniently employed in determining the departure of the gas from Boyle's Law. In particular, the ratio $(pv)_0/(pv)_1$ can be calculated, so that, from the values relating to the normal density and compressibility of phosphine, the molar weight of the gas and the atomic weight of phosphorus can be determined.

[*] 'C. R.,' vol. 126, p. 1415 (1898).

[†] 'C. R.,' vol. 125, p. 297 (1897).

[‡] *Cf.* Gray, 'Trans. Chem. Soc.,' vol. 95, p. 1657 (1909).

General Description of Methods and Apparatus.

Both the density and compressibility were determined by the density-globe method, *i.e.*, by weighing a known volume of gas under known conditions of temperature and pressure. Density determinations were carried out at four distinct pressure levels, *viz.*, one atmosphere, three-quarters atmosphere, one-half atmosphere, and one-quarter atmosphere, the temperature in every case being that afforded by crushed and moistened ice. Two density globes of the ordinary stopcock type were employed throughout the experiments. Each was, roughly, 350 c.c. in volume and 80 grm. in weight, being constructed of ordinary soft glass, fairly thick in the wall to reduce the correction for contraction on evacuation. The actual contraction per atmosphere was about 0·02 c.c. Each globe was provided with a counterpoising bulb whose external volume differed from that of the corresponding globe by less than 0·2 c.c. These counterpoises were, as far as possible, subjected to the same treatment as the globes. They were constructed of the same glass as were the globes and in their final forms were about 3 grams lighter in weight.

The weight of the empty globe was calculated by weighing the globe with a known internal pressure of 0·5 to 1·5 mm., accurately measured by means of a McLeod gauge; so that, from a knowledge of the approximate density at low pressures, a sufficiently exact figure was obtained for the weight of gas remaining in the globe.

The higher pressures of 760 mm., etc., were measured by means of a manobarometer attached directly to the apparatus, the mercury levels being observed by a cathetometer reading nominally to 0·05 mm. This barometer was also employed to check the readings of the vacuometer.

Weighings were carried out by means of a Staudinger balance with an accuracy of 0·02 or 0·01 milligram. The weight of gas involved ranged from 0·52 gram at one atmosphere to 0·13 at one-quarter atmosphere. At least 15 hours were allowed to elapse from the removal of the globes and counterpoises from the ice (with the consequent wiping and washing) and the actual time of weighing. Three weighings were, in general, recorded.

The weights employed in the actual density determinations and in the volume standardizations of the globes were carefully calibrated against each other. The fractional weights were of platinum. It is not necessary that the weights should be standard weights, provided the units of weight and volume are concordant.

Description of Apparatus.

A diagram of the actual apparatus employed is given herewith. It is constructed entirely of soft glass, with the exception of the rubber stopper of the generating flask Q, and the rubber joints used to attach the density globes I and II. Briefly, phosphine was prepared from phosphonium iodide crystals and dilute potassium hydroxide solution in the flask Q, passed through potassium hydroxide solution in the wash-bottles W, over solid potassium hydroxide in the small tower *t*, and collected in the solid form by means of liquid air in bulb A. The gas was then distilled through the drying-tubes T and D, the former containing potassium hydroxide lumps and the latter phosphorus pentoxide, and was collected in bulb C as before. Glass wool in H prevented the transference of mechanically carried particles from the pentoxide, and the millimetre capillary tube which followed served to check any sudden change in the rate of flow of the gas through the drying-tubes. The gas after drying was distilled several times between bulbs B and C, first and final fractions being rejected, and was finally collected in bulb B ; so that the first part of the apparatus up to tap 9 served for the preparation of the pure and dry gas. The rest of the apparatus served for the filling of the density globes, at 0° C. and at

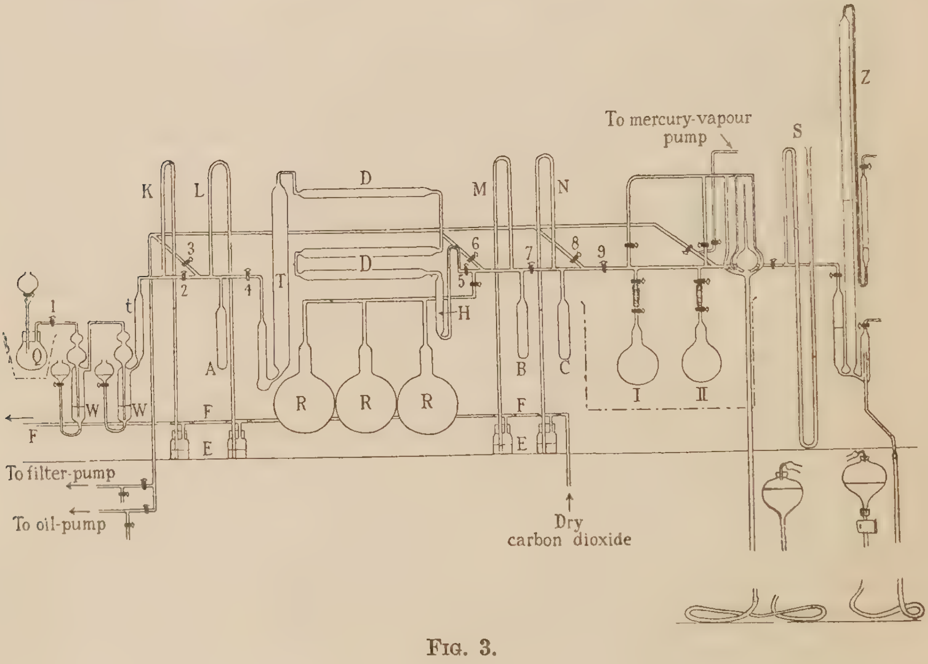

Fig. 3.

known pressure, indicated approximately by the manometer S, and measured exactly by the mano-barometer Z.

The three globes R, each of about 700 c.c. volume, acted as reservoirs for gas prepared and purified but not used in a filling, any such gas left over from one experiment being, of course, subjected to further fractional distillation before being used. The safety manometers K, L, M and N, dip into mercury in the closed bottles E, a slow current of dry carbon dioxide being passed along the outlet-tube F into the fume cupboard.

The tap grease used throughout the experiments on all stopcocks was a rubber grease, which proved most satisfactory. It did not appear to be noticeably attacked by phosphine gas ; a slight thickening in consistency was the only change after months of use. Globe stopcocks were regreased once during the actual density experiments.

For evacuation purposes, three pumps in all were employed, an ordinary water filter-pump, a rotatory oil pump driven by an electric motor, and a mercury-vapour pump. The oil pump was capable of producing a pressure of less than 0·001 mm. in a very short period of time, but, of course, could not be employed generally for the removal of phosphine gas. Where possible, the filter-pump was applied, the oil pump being only used occasionally on phosphine when the pressure was very low. Liquid air also was frequently employed, the vapour pressure of solid phosphine at the temperature of liquid air being less than 0·05 mm. Hg. The mercury-vapour pump was only used for the removal of the last traces of air.

Phosphorus Pentoxide Tubes.—In view of the importance of obtaining a thoroughly dry gas, particular attention was paid to the filling and sealing into position of the drying-tubes. These were of a total length of from 4 to 5 feet and of 15 mm. diameter. The phosphorus pentoxide was interspersed every 2 inches with 1-inch lengths of glass-wool, this form of drying tube being used in the actual density determinations. The phosphorus pentoxide was packed fairly tightly into the tubes to offer as large a surface as possible to the moving gas. The three tubes were replaced after about six experiments. In filling and sealing into position, every precaution was taken to prevent the presence of any moisture.

After these drying-tubes were placed in position, they were kept for several days at as low a pressure as possible, thus serving the double purpose of testing for leaks and of freeing the phosphorus pentoxide of adsorbed or entrapped air. Noyes[*] mentions also the possibility of the glass-wool consisting of glass tubes from which air might only be slowly removed. Even after 3 or 4 days' evacuation, some such air always seemed to be present, since on standing with phosphine the pentoxide acquired very slowly (after a month or so) a yellowish tint, and some gas was produced, not condensed by liquid air, and therefore probably hydrogen. For this reason a distillation with drying cannot be regarded as so efficient as a simple distillation, unless special precautions have been taken; it is to be expected also that the yellow coating on the pentoxide particles would prevent proper drying of the gas.

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[*] ‘Amer. Chem. J.,’ vol. 11, p. 156 (1889).

Mano-barometer.—This instrument was constructed entirely of soft glass, being of the type described by Germann.* The dimensions used were sensibly the same as those adopted by him, the internal diameter of the main short and long limbs being 18 mm. Both limbs were constructed from the same glass tube, and as observations were always carried out after causing the mercury to rise slightly in both limbs simultaneously, no meniscus correction was applied. No stopcock was employed between the air-trap and the rubber tubing leading to the moveable mercury reservoir; in this way, the barometer was filled and used without the mercury coming into contact with any greased surface. The air-trap was sealed into position in such a way, that the internal seal was well below the foot of the manometer proper; in this way, complete and proper evacuation can be given. Two clamps were employed on the rubber tube of the mercury reservoir, one a large wooden clamp 2 inches wide, which also served to support the rubber tubing, and the other a small screw-clip, used in the final adjustment of the mercury surfaces. The best heavy-pressure rubber tubing was used for the connection.

The cleaning, drying, and filling of the mano-barometer were carried out on the usual lines (*cf.* Germann, *loc. cit.*). To facilitate the initial operations, a subsidiary stopcock was temporarily sealed into position below the air-trap. Drying was accomplished by alternate evacuation and filling with dry air. Before the filling with mercury was begun, the main limbs were subjected to mercury-vapour pump exhaustion for 5 days. After filling, no difference in mercury levels in the two limbs could be detected by the telescope of the cathetometer on connecting the barometer "gas-space" to the mercury-vapour pump; the barometer was therefore sufficiently accurate for the purpose. In each density experiment, the vacuum was tested in the usual way by raising the mercury reservoir sufficiently; at no time was more than a mere trace of gas to be obtained.

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* 'J. Phys. Chem.,' vol. 19, p. 437 (1915); 'J. Chim. Phys.,' vol. 12, p. 78 (1914).

The barometer itself was shielded on either side by large asbestos sheets; the temperature of the mercury was taken as that given by two standard thermometers reading to 0·01° C., hung by the side of the main limb, one with its bulb half-way up, the other with its bulb slightly above the junction of the two limbs. It may be mentioned here that, as a period of 2 hours free from disturbance elapsed before readings of pressure and temperature were recorded, sudden fluctuations in the temperature readings were not observed. A slight fall in temperature during the readings of the pressure was generally recorded on both thermometers, the usual difference being about 0·05° C. during the period of time thus occupied (half an hour). The cause was probably the proximity of the ice-bath for the globes. The average of the temperature readings was employed in the density calculations.

The mercury levels in the gas space were at the same vertical height as the centre of the globes; no correction on this account need be applied.

When the barometer was not in actual use, it was advisable to evacuate the gas-space. After allowing phosphine at one atmosphere to stand for several weeks in the barometer gas-space, the pressure could not at once be reduced below 0·05 to 0·08 mm. At the same time, pressure readings by vacuometer were lower than readings by barometer. Continued evacuation, however, equated the mercury levels of the barometer, so that, after such filling and measurements of pressure, the barometer gas-space was evacuated at once. The correct zero level was then attained immediately. The only explanation put forward is that the grease of the stopcock adsorbs at first a small amount of gas, and that part of this gas, or some decomposition product, can be removed slowly by exhaustion.

Cathetometer.—This instrument was the "Universal" model of Casella & Company, London. By paying particular attention to the setting of the telescope and telescope stage, it was possible to record a series of readings of the same pressure without more than 0·05 mm. difference between the "outside" readings; by averaging, therefore, an accuracy of more than 0·05 mm. was expected. At each reading (about a dozen readings of the same pressure being recorded) the temperature of the cathetometer scale was observed by means of two thermometers to 0·1°. Behind the actual meniscus of the mercury column of the barometer a card was placed, sharply divided horizontally into two white and black sections.* If the line of division be placed 1 or 2 mm. above the meniscus, with the black section uppermost, the mercury surface appears as a dead-black line, easily brought to coincidence with the cross-wire of the telescope. Two such cards were employed, one for each mercury surface; each was placed at the same distance above the surface (1–2 mm.), although no apparent difference in level could be observed, if, for example, the dividing edge of the card were placed 2 mm. instead of 1 mm. above the surface.

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* *Cf.* Travers, Senter, Jacquerod, 'Phil. Trans.,' A, vol. 200, p. 111 (1903).

Through the kindness of Prof. R. A. Sampson, of the Royal Observatory, Edinburgh, the brass scale of the cathetometer was calibrated by comparison with a standard metre. The scale was almost exactly correct at 15° C. A correcting factor of 1·0004 (1) was accordingly applied to the length of the scale at 0° C.

Vacuometer.—The vacuometer was of the standard McLeod type where 100 c.c. gas at the original unknown pressure can be compressed into a graduated capillary of total volume 1·5 c.c. This instrument, used to measure pressures of 0·5 mm. to 1·5 mm., always gave definite and constant results when employed with the necessary precautions.* Cleaning and drying were carried out in the same way as in the case of the barometer. Thorough drying is essential; during the operations no carbon dioxide was admitted to the apparatus.† It was normally kept at a pressure less than 0·5 mm. of phosphine, the main mercury reservoir being so adjusted that the remaining gas was completely trapped by mercury in the main 100 c.c. bulb. The chief precaution in its use appeared to lie in the very slow rise of mercury when a reading was being taken. Otherwise, gas appears to be trapped by the rising mercury on the sides of the bulb; an error of 0·03 mm. may be caused in this way. In general, with all precautions for the usual range of pressures from 0·5 mm. to 1·5 mm., the vacuometer gave readings of 0·01 to 0·04 mm. less than corresponding readings by the barometer, this discrepancy being apparently due to the above-mentioned trapping of gas or to the tendency of the barometer to give high readings at low pressure (*cf.* p. 557). The average of all barometer and vacuometer readings was generally taken. An error of 0·02 mm. in the reading corresponds roughly to 0·01 milligram of gas when applied to the weight of the globe taken at the reduced pressure.

Mercury.—The mercury used in the various measuring instruments and manometers, after filtration through muslin, was twice passed through an ordinary nitric acid purifier, kept for some time at 80° C. and then twice distilled under a reduced pressure of approximately 12 mm. in a barometric still. Half of it was later redistilled in the ordinary way with air-leak and condenser, the pressure being reduced by filter pump. Pure and dry phosphine remains in contact with such mercury for an indefinite period without any signs of decomposition.

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* *Cf.* Baume, 'J. Chim. Phys.,' vol. 6, p. 1 (1908); Travers, "Study of Gases," p. 158; Baly and Ramsay, 'Phil. Mag.,' vol. 38, p. 318 (1894).

† Baly and Ramsay, *loc. cit.*

Rubber joints were always used to attach the density globes to the main apparatus. They were cut from the best heavy-pressure rubber tubing and the talc, etc., removed as far as possible from the inside surface by moistening with water and rubbing with a glass rod cut square across. While moist, they were slipped into position on the apparatus, doubly wired on, the globes similarly put into position, and then all air and moisture thus introduced removed by thorough evacuation (30 minutes to an hour) by oil-pump. The removal of the water is a most essential precaution ; the importance of such exhaustive drying has been emphasized by Scheuer.* Treated in this way, such joints were always satisfactory, no leakage or other change of pressure being detected ; the action of phosphine gas on the small area of rubber exposed would appear to be entirely negligible.

Seals.—In order to prevent leakage into the globes during the drying period when the internal pressure was less than atmospheric pressure, seals were always applied. In the case of the very low pressures 0·5 to 1·5 mm., a short length of clean rubber tubing, wired to an extension piece of glass tubing, was slipped on, all moisture being removed by oil-pump as before, and then the glass tube sealed off while evacuated. The pressure inside the outer tap-stem was thus less than 0·1 mm. ; leakage from the outside was effectively prevented, and if any change in pressure occurred inside the globe, it would be the very small reduction due to leakage from the globe into the evacuated extension. The same principle was employed for the other pressures (quarter atmosphere, etc.), except that, after evacuation to remove moisture, dry air was allowed in until the pressure of air in the tap-stem was a few millimetres less than the pressure of phosphine in the globe. Such seals were, of course, removed before weighing ; during the period of weighing, inleakage, if any, was inappreciable.

Standardization of the Density Globes.

The standardization of the globes can be considered in three sections ; the determination of the contraction in volume on evacuation, the counterpoising, and the determination of the internal volume.

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* 'Z. Phys. Chem.,' vol. 68, p. 592 (1909).

Contraction in Volume on Evacuation.

The method adopted was the direct Travers method,* a large double thick-glass desiccator being employed, and the whole being immersed in a constant-temperature water-bath. In the usual way, it was ascertained that the contraction in volume varied linearly with the reduction in pressure; the contraction for globe I was 0·017 c.c. per atmosphere and that for globe II 0·019 c.c. per atmosphere. The correction applied to the weight of gas in a one-atmosphere pressure determination was thus 0·00002 (0) grm. for globe I, and 0·00002(3) grm. for globe II, the weight of 1 c.c. of air being taken as 1·2 mgrm. An error of 1 cm. in the reading of the capillary in the experiment is equivalent to a weight-error of 0·00000 (25) grms.; it is very improbable that such an error is involved in the experiment.

Counterpoising.—The volume of globes and respective counterpoises were compared in the usual way by weighing in air and weighing in water. By trial and repeated adjustment of a small auxiliary bulb attached to the counterpoising bulb, an almost exact volume-counterpoise was obtained. Thus for globe I and globe II, the difference in weight of displaced water between globe and counterpoise was respectively 0·14 grm. and 0·12 grm. Globes and respective counterpoises thus agreed in external volume to less than 0·2 c.c.

Volume of the Globes.

The determination of the internal volume of the globes was carried out in the lines recommended by Germann.† The distilled water used was boiled for 1 hour as a preliminary and the time of cooling in ice was from 4 to 5 hours. After removal from the ice, the globes were washed with distilled water, wiped carefully with clean, moist muslin, and again washed and sprayed with distilled water. They were then suspended by aluminium wire in a closed cupboard containing a basin of phosphorus pentoxide. Counterpoises were treated in an exactly similar fashion. After hanging for half an hour, any drops of water were removed from the bottoms of the globes and counterpoises by means of filter-paper. After 15 hours, weighings were carried out to the nearest milligram (by means of the Staudinger balance). Temperature and pressure were recorded at the same time. A similar procedure as to washing, cleaning, drying, etc., was carried out for the evacuated globes, the "seals" which had been in position during the drying period, being, of course, removed before weighing. The residual pressure was less than 0·1 mm. Hg, and the weight of air remaining in the globes consequently negligible.

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* Travers, "Study of Gases," p. 120; Germann, 'J. Phys. Chem.,' vol. 19, p. 463 (1915); *cf.* Moles and Miravalles, 'J. Chim. Phys.,' vol. 21, p. 1 (1924).

† *Loc. cit.*; *cf.* Baume, 'J. Chim. Phys.,' vol 6, p. 1 (1908).

Results were as follows :—

	Globe I.		Globe II.
	335·523 grm.		341·292 grm.
	335·518 ,,		341·294 ,,
	335·520 ,,		341·290 ,,
	335·520 ,,		341·294 ,,
Average	335·520 grm.	Average	341·293 grm.

The weight of water at 0° C. required to fill globe I was therefore 335·520 grm., and the corresponding figure for globe II, 341·293 grm. These values refer to the corrected weights used, reduced to a vacuum standard, under the value of g, the acceleration due to gravity, at the laboratory.

Since the contraction in volume of the globes was about 0·02 c.c. per atmosphere, the above figures were altered accordingly for the purposes of the calculation of the densities at the various pressures. The correction is a small one, being at the most of the order of 1 in 20,000.

Travers has mentioned the fact that density globes, especially when newly constructed, have a distinct tendency to decrease in volume.* Accordingly, at the conclusion of the density experiments, 12 months after the calibrations, the volumes of the globes were re-determined. The values then obtained for the weight of water at 0° C. were for globe I, 335·502 grm. and for globe II, 341·274 grm. These figures represent a decrease of about 1 in 15,000. It may be of interest to state that the density globes were constructed at the beginning of this investigation, although, the possibility of such contraction being in mind, they were kept in a fully exhausted condition for more than a fortnight before the determination of the internal volume was begun. The density experiments were carried out at three distinct and approximately equal intervals of time, so that the actual figures employed in the density calculations were adjusted on the assumption that the decrease in volume was proportional to the time elapsing from the original calibration.

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* "Study of Gases," p. 119 ; *cf.* Scheuer, 'Z. Phys. Chem.,' vol. 68, p. 588 (1909).

Preparation of Phosphonium Iodide.

The phosphonium iodide used in the preparation of the phosphine gas was prepared by a modification of the method given by Baeyer.* The reaction is generally represented by the equation

$$9P + 5I + 16H_2O = 5PH_4I + 4H_3PO_4.$$

In the final stages of the preparation, *i.e.*, during the addition of the water to the iodide of phosphorus, the phosphonium iodide was not allowed to sublime out from the reaction mixture, but was retained therein by surrounding the flask with ice. After the addition of the necessary water, the mixture was set aside for 3 or 4 days, and the iodide subsequently sublimed out by heating in water at 80° to 90° C. More water was then added to the residue and the contents allowed to remain a few days before sublimation was again begun. The iodide was prepared in small portions of 100 grm. at a time, from 60 grm. white phosphorus and 100 grm. iodine. The yield obtained from these quantities in the ordinary way would appear to be about 70 grm.; by repeated treatment of the "residue," as above, the actual yield was always greater than 100 grm. The theoretical yield is 127 grm. iodide from 100 grm. iodine.

The crude yellowish-brown iodide thus obtained was resublimed at 50° C. to 70° C., the pressure being initially reduced by filter-pump as far as possible. The product was then obtained in transparent cubic crystals. This "purified" iodide† was used in the preparation of the phosphine gas for the density determinations.

Preparation of Pure Phosphine.

Initially, all air was removed from the sections of the apparatus following tap 1 (see fig.) by means of the mercury-vapour pump. The generating flask was then filled with carbon dioxide, about 40 grm. iodide were added and the flask put into position. After opening tap 1, tap 2 being closed, dilute KOH solution was run into the wash-bottles. The descriptions that follow apply in general to the ordinary cases where each section contained gas left over from a previous experiment.

KOH solution (20 per cent.) was added drop by drop to the solid iodide, and phosphine gas was consequently evolved at a rate easily observed by the mercury manometer K. The action was regular and easily controlled, the pressure remaining practically steady whenever the supply of hydroxide solution was interrupted. Flask Q was surrounded by ice to reduce as far as possible the percentage of hydrogen and other hydrides of phosphorus; for the same reason 20 per cent. KOH solution was employed to liberate the phosphine itself. The same solution was used in the gas wash-bottles; this was renewed when necessary following filter-pump suction applied to the dropping funnels. The first wash-bottle was also cooled in ice, although the action of phosphine on potassium hydroxide solution is taken to be small.*

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* Liebig's 'Annalen,' vol. 155, p. 269 (1870).

† *Cf.* Holt and Myers, 'Z. Anorg. Chem.,' vols. 82, 83, p. 279 (1913).

The gas was collected in the solid form in the bottom of bulb A by means of liquid air. Taps 3 and 4 were, of course, closed, while tap 2, connecting the generating section and the collecting bulb, was kept only partially open, so that the pressure in the generating section was about three-quarters of an atmosphere, while that in the bulb was very low. This pressure in A, as shown by the manometer L, tended to increase somewhat as the gas continued to collect in A, owing to the presence of hydrogen or nitrogen. The vapour pressure of solid phosphine at the temperature of liquid air is less than 0·05 mm. Hg; the "excess" pressure, if large, was reduced at intervals by means of the filter-pump acting through tap 3. When no more gas could be obtained from the quantity of iodide used, tap 2 was closed; the contents of bulb A were then employed in the subsequent purification.

This preparation of phosphine was carried out slowly. For the quantities used, from 2 to 3 hours were usually given; otherwise a yellow solid residue was left behind in bulb A after distillation. This residue could be entirely avoided if sufficient time were given to the preparation.

The crude phosphine was now ready for purification, but before this was begun the phosphine in the other sections of the apparatus (drying tubes, reservoirs, bulbs) was also solidified in bulb A. The other sections were then evacuated as far as possible by oil-pump. All the phosphine in the bulb was now purified by drying and fractionation.

The solid phosphine was allowed to liquefy by lowering slightly the vacuum vessel containing liquid air. Total withdrawal with free exposure to the outside air may cause sudden and violent changes of pressure, especially if the solid phosphine be on the sides of the bulb instead of at the bottom. When all had assumed the liquid form and the pressure had reached about half an atmosphere, the first fraction of one-fifth of the total volume was allowed to evaporate and was rejected by means of the filter-pump. Slow and steady evaporation was ensured by surrounding the bulb by a vacuum flask containing a little liquid air. Finally, the manometer tubes were washed out by allowing gas to escape by the mercury bottle E, a current of dry carbon dioxide being passed along the exit tube, F, at the same time ; this prevented any possibility of explosion. The remaining phosphine was then resolidified.

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* *Cf.* Mellor, "Inorganic and Theoretical Chemistry," vol. 8, p. 816.

Distillation was then conducted through the drying tubes into bulb C. Tap 5, which directly follows these drying-tubes, was kept only partially open, so that the pressure in the drying-tubes and in the bulb A was always kept between three-quarters and one atmosphere, while that of the bulbs B and C always remained very small and close to the vapour-pressure of solid phosphine at the temperature of liquid air. By closing tap 7, the rate of flow of gas through tap 5 could at once be observed by the slow fall of mercury level in the safety manometer M ; in this way, an exact control was kept of the process of the distillation. Distillation was continued until about one-fifth of the original volume in bulb A remained ; the residue was rejected by means of the filter-pump through tap 3. The period of distillation was from 6 to 8 hours ; a perfectly colourless glassy or crystalline solid, melting to a clear and colourless liquid, was always obtained.

The process of simple distillation was then carried out backwards and forwards between bulbs B and C, the collecting bulb being well washed out with fresh gas before actual solidification was begun. Beginning and end fractions were rejected as before. During a distillation, the collecting bulb was surrounded by liquid air, the intermediate tap being kept only partially open, and the pressure in the collecting bulb, as indicated by the appropriate manometer, being very low. The pressure in the distilling bulb, on the other hand, was kept at one-half to one-quarter atmosphere by suitably raising or lowering a vacuum vessel containing a little liquid air ; this pressure was also varied by means of the connecting stopcock. The number of such distillations given was usually three or four, followed by a fifth when actually filling the globes ; it was found that, after the second distillation, the pressure over the solid phosphine at the temperature of liquid air reached a practically constant value.*

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* Prof. H. B. Baker, in a private communication, kindly informs me that he has observed a partial decomposition (into hydrogen and the liquid hydride P_2H_4) of phosphine which had been submitted to expansion and subsequent compression. Under the conditions of filling described above, the extent of such a decomposition can only have been very small, as the following observations show.

It was stated above that gas prepared and purified, but not used in a filling, was collected in the reservoirs R, which were of a total capacity of roughly 2200 c.c. These reservoirs were evacuated as far as possible by oil-pump before being used for gas storage. The process of filling them was similar to the filling of the density globes. Such gas, treated shortly after storage, was on several occasions solidified by liquid air in one of the evacuated

When a distillation was conducted under the above conditions, the time occupied was from 2 to 3 hours. If the distillation were conducted from a bulb freely exposed to the air, the time was then less than 1 hour, but the collected distillate was not colourless, but greyish when solid and of a slate-blue colour when liquid. This darkening in colour was due to solid black particles floating throughout the liquid, and no improvement was effected by repeated distillation under similar conditions, although these solid particles were in the main left behind in a distillation. At the same time, it became more difficult to obtain a constant pressure over the solid phosphine; the effect was as if a non-condensable gas, such as hydrogen, were present in varying quantities, the different temperatures and pressures occurring in such an "air-exposure" distillation appearing to facilitate decomposition of phosphine into hydrogen and some solid compound. Under such conditions, therefore, no increase in the number of distillations given would improve in any way the purity of the product.

Reference may be made here to the method adopted in the rejection of the initial fraction. It had been originally intended to reject such gas by means of the mercury cups closing the manometers. Unless these cups were well filled previously with carbon dioxide and a current of gas passed continuously, the phosphine rejected was liable to explosion; one such explosion necessitated the complete replacement of that section of the apparatus. This liability of phosphine gas to spontaneous combustion in air appears to be determined by the following conditions. Firstly, the gas is spontaneously inflammable if it contains, at a given temperature, more than a certain percentage of the hydride P_2H_4. When this percentage falls below the limiting value, the gas is not spontaneously inflammable, if the additional condition be introduced, that

bulbs B or C. The initial pressure of gas was atmospheric; the final pressure after solidification was less than 0·1 mm. as measured by vacuometer. Assuming this pressure to be due entirely to hydrogen, the weight of a volume of 2200 c.c. impure gas at atmospheric pressure would be 0·00041 grm. less than the corresponding weight for pure phosphine, and therefore the error in the globe volume of 350 c.c. (weight of gas about 0·5 grm.) would be less than 0·00006 grm., representing a difference of 1 in 8000, comparable to the error liable to be introduced in a globe weighing.

Again, as mentioned later, an actual density determination was carried out using the method of purification involving bubbling of the gas through liquid phosphine. In preliminary trials, solid carbon dioxide and ether (under atmospheric pressure) were used in an attempt to liquefy a sufficient quantity of phosphine in the bubbler. The temperature reached was, however, slightly too high for the purpose, and no condensation took place; careful observation showed no trace of deposit, liquid or solid, although the temperature was sufficiently low to condense traces of P_2H_4 had they been present.

the gas be moist, *i.e.*, that it contains more than a certain percentage of water vapour. This is the stage represented in the generating section of the apparatus; such gas was not, as a rule, spontaneously inflammable, in agreement with the observation of Rammelsberg* that phosphine liberated from phosphonium iodide by dilute potassium hydroxide solution is not usually spontaneously inflammable but is occasionally so. Lastly, when dried† by stick potassium hydroxide and phosphorus pentoxide, in the manner indicated above, the gas was always spontaneously inflammable in the air. The rejection of gas from the apparatus was, therefore, as far as possible carried out by means of the filter-pump, which moistened the gas sufficiently to render it non-inflammable. The conditions given above do not, of course, include many other complicating factors that are not mentioned; for example, a mixture of phosphine, air and water-vapour, which would be stable at atmospheric pressure, might not be stable at one-quarter atmosphere pressure. This was occasionally made evident in preparation of the gas, when the gas at the pressure of the generating section (three-quarters atmosphere) passed through the connecting tap into a section kept at a low pressure by means of liquid air. Slight explosion then occurred if more than a trace of air were present in the generating section.

The main bulk of rejected gas in a distillation was, therefore, withdrawn by means of the filter-pump. It was advisable, however, that the manometer outlets be employed occasionally; the hydrogen which appeared to collect in the top bends of these manometer tubes was otherwise difficult to remove satisfactorily. When a slow current of carbon dioxide is employed in the exit tube to sweep out such rejected gas, care must be taken; a sudden reduction of pressure in any distilling bulb (by the application of liquid air, for example) may draw sufficient air into the exit tube to cause explosion. For this reason, as well as to reduce the quantity of hydrogen in the bulb, these manometers are best constructed of small-diameter tubing.

Such are the main details in connection with the preparation of pure and dry gas. Provided a very slow distillation was carried out in the actual filling of the density-globes, the final product was considered free from hydrogen and the other impurities liable to be introduced in the actual preparation of the phosphine. The solid phosphorus used in the original preparation of the phosphonium iodide was examined for arsenic, since arsine might be difficult to separate from phosphine by simple distillation. It is not likely, however, that arsenic would be carried past the iodide stage of the preparation. By Marsh's test it was found that the arsenic content of the original phosphorus was less than 1 in 100,000 and as such was not likely to affect the density figures.

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* 'J. Chem. Soc.,' p. 601 (1873).

† *Cf.* Abegg's "Anorg. Chemie," vol. 3, p. 395.

It was originally intended to submit the gas to further purification* by bubbling through liquid phosphine. This was actually done on one occasion, but no increase in purity could be detected as judged by the density results in this experiment ; reliance was therefore placed on simple distillation for the purification.

Experimental Procedure in Density Determinations.

Preliminary Treatment of Density Globes.—It is of the utmost importance that the internal surfaces of the globes be entirely free from moisture. To this end, after thorough cleaning and careful regreasing of the stopcocks, repeated evacuation and filling with dry air was carried out, the mercury vapour pump being used in the final stages. Lastly, the globes were subjected to mercury-pump exhaustion for 3 days ; the surfaces were then considered to be in a suitable condition for saturation with the pure and dry gas. A supply of pure phosphine was prepared by the methods already described, and both globes were slowly filled with the gas until the internal pressure was roughly atmospheric. After closing all taps, the apparatus was left for 4 to 5 days in the hope that satisfactory equilibrium would be obtained in that period.

Evacuation.—The next step was to obtain the weight of the "empty" globe, *i.e.*, to find the weight of the globe containing gas at a known pressure of about 1 mm. For this purpose, both globes were surrounded by cleanly crushed ice, which was kept at a level above the stopcocks of the globes, melted ice being allowed to run out through holes in the bottom of the ice-box. The counterpoises were embedded in the same ice. Globes and counterpoises were subjected to the same treatment in a "reduced-pressure" determination or "evacuation" as in a "filling" at atmospheric or other standard pressure, all such processes being duplicated as far as possible. The globes and counterpoises were, therefore, surrounded by ice 1 hour before filling or evacuation, followed by a period of 2 hours given to ensure thermal equilibrium before the final measurements were begun.

The internal pressure was accordingly reduced to approximately 1 mm. In order that no inleakage should occur during the period given for the attainment of equilibrium, the sections adjacent were also reduced to roughly the same pressure. After adjusting the level of the mercury in the vacuometer so that it was just below the opening into the main bulb, the apparatus was left for 2 hours to attain equilibrium. This length of time was mainly given because such is the period required in the corresponding filling of the globes; in the present case, equilibrium appeared to be attained in a very much shorter time. At the end of 1 hour, the mercury surfaces of the barometer were subjected to the same upward movement; the clips were then tightly fastened on the rubber tube leading to the mercury reservoir. Near the end of the second hour, readings by vacuometer and barometer were taken alternately. Provided the experiment was carried out as above, no trouble was experienced; fluctuation in pressure can only be ascribed to imperfect drying of the rubber joints or to inleakage from adjacent sections.

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* *Cf.* Reiman, 'J. Chim. Phys.,' vol. 15, pp. 292, 345 (1917) ; Gray, 'J. Chem. Soc.,' vol. 87, p. 1605 (1905).

After a series of pressure readings, the globe stopcocks were finally closed and the pressure elsewhere reduced, first by liquid air and then by oil-pump, before the rubber joints were cut off; otherwise the admission of air might cause burning, with deposition of oxides and acids of phosphorus in the tap stems of the globes. Following the cleaning of the tap-stems, outside and inside, of all sediment from the rubber joints, seals (*cf.* p. 559) were slipped into position, all air and moisture thus introduced being removed by evacuation. While evacuated, the connection to the pump was sealed off; globes and counterpoises were then wiped with moist muslin and sprayed with distilled water before being hung in the drying cupboard, prior to weighing. As before, after a short time, any drops of water were removed from the bottoms of the vessels, then a basin containing phosphorus pentoxide put inside and all allowed to remain undisturbed for at least 15 hours before weighing.

Filling.—After the weighings of the "empty" globes were completed, the globes were reattached to the apparatus and the air and moisture thus introduced removed by thorough exhaustion by the oil-pump. Increase of pressure was then tested for by means of the vacuometer, over a period ranging from half an hour to an hour. The joints being pronounced satisfactory, the globes (and counterpoises) were surrounded by ice; everything was then in readiness for the filling.

The phosphine, dried and fractionated as already described, was held in the solid form in bulb B usually. After rejection of a large initial fraction, the globes were washed out three or four times with fresh gas, these washings taking the form of fillings to half an atmosphere pressure, alternated by filter-pump evacuation. At this stage, also, the barometric vacuum was checked by driving over some mercury from the main limb to the capillary reservoir. Finally, the pressure in the globes was very slowly allowed to increase until the required pressure was attained; adjacent sections were similarly treated (with exception of the vacuometer) before the apparatus was allowed to stand to attain equilibrium. After 1½ hours the mercury surfaces of the barometer were subjected to the same upward movement; at the end of 2 hours, readings of the pressure were begun. During this period, the ice used was kept well packed round the globes, being moistened occasionally with distilled water while the level of the ice was kept well above the stopcocks of the globes. A thermometer reading to hundredths of a degree was also placed in the ice; the temperature here recorded was in every experiment practically constant.

After the expiry of the 2 hours, the readings were begun, first by taking the temperature of the ice, followed by the thermometer readings on the barometer itself and on the cathetometer scale. The actual difference in mercury levels was then observed, repeated observations being taken; after the final reading, the globe stopcocks were quickly closed and the temperatures again all recorded. The globes were then cut off after evacuation of all other sections, including the barometer gas-space. Appropriate seals were then applied to the globes, if necessary, *i.e.*, if the internal pressure of the globes were one-quarter, one-half, or three-quarters atmosphere. Globes and counterpoises were then washed and hung away in the drying cupboard prior to weighing.

Weighings.—The procedure in connection with the weighings is one on which too much importance cannot be laid. It must be remembered that at one-quarter atmosphere pressure the weight of gas in the globe was only slightly greater than one-tenth of a gram; to attain an accuracy of 1 in 10,000, therefore, weighings would need to be exact to 0·01 milligram, without taking into consideration the fact that the object actually on the balance pan might not represent the true weight desired, by reason of grease, dust particles, and the like, picked up in various stages of the experiment.

The balance used was the Staudinger balance previously employed in the determination of the volume of the globes. The balance case was partially covered with tin-foil to minimize the effects of unequal temperatures. The sensitivity with globe and counterpoise in position was about 1·5 scale divisions per milligram; by means of a telescope fixed in the case, readings of the resting-point could be taken to the nearest hundredth of a division. A thermometer, reading to 0·01° C., was hung inside the balance case in a central position, this being assumed to give the actual temperature during a weighing.

Without doubt, the most important factor in the determination of the weight of an object on the balance-pan is the factor of temperature. Apart from the effects of unequal temperatures, occasioned by air-currents or other such disturbances, the resting-point of the balance beam depended on the temperature inside the balance case; a definite temperature coefficient* was obtained, whereby, for a given load, the resting-point could be corrected to a given temperature. Every attempt was made to render such a correction as small as possible.

As mentioned previously, weighings were carried out after at least 15 hours' suspension of globes and counterpoises in the drying cupboard, this suspension being accomplished by means of aluminium wire loops, which were not removed at any time and which served to support the globes and counterpoises on the balance pans. "Seals" which had prevented entry of air into the globes during the drying period were cut off, the globes being held at the stem by means of silk finger-covers; the tap-stems were very carefully cleaned by dry muslin, and then all visible dust particles removed from the bulbs by touching lightly with a small brush. In this condition, transference to the balance case could be accomplished, the globe being placed on the left-hand pan and the counterpoise and necessary weights on the right-hand pan.

The zero-point was determined with a 20-gram weight on each scale pan, the weights being so distinguished that a particular weight always occupied the same pan. These weights were removed when the globe and counterpoise were introduced. The zero-point was first determined, then the resting-point with globe and counterpoise in position, then again the zero-point. In each case, after the insertion of the weights, the balance case was allowed to remain closed for 10 minutes; the beam was then released and allowed to swing for 10 minutes; finally, the beam was arrested and reswung, the resting-point being recorded by means of repeated and continuous swings. The temperature in the case was observed at the same time. The sensitivity with globe and counterpoise in position was determined at each weighing.

These observations gave two zero-points at two corresponding temperatures with a resting-point for the globe at an intermediate temperature. From the zero-point temperature coefficient thus obtained (always about $-0 \cdot 25$ scale divisions per degree) the true zero-point at the intermediate temperature was calculated, from which by the sensitivity the required weight was obtained. The atmospheric pressure was also recorded for the purpose of reducing the weight obtained to the vacuum standard.

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* *Cf.* Manley, 'Phil. Trans.,' A, vol. 210, p. 401 (1910).

The seals were immediately replaced if repeat weighings were to be carried out later.

For concordant readings of the resting-point at the same temperature it was essential that release and arrestment of the beam be carried out with the greatest care. Sudden arrestment might alter knife-edges, etc., or alter the position of the rider on the beam. Sudden release might cause an appreciable difference in resting-point, due to a different position of the knife-edge. The procedure adopted was to release the beam as gently as possible, no attempt being made to swing the beam ; this was then accomplished by the temporary application of an additional rider. In this way alone would concordant results be obtained.

The weights used were calibrated against each other in air by the substitution method of Richards.[*] Every attention was paid to such calibration, especially with regard to the fractional weights ; successive figures for a given weight, differing by more than 0·01 milligram, were seldom obtained.

Results of Repeat Weighings.—Weighings were carried out in the morning of the day after the globes were washed, in the late afternoon of the same day, and on the morning of the following day. The following figures refer to weights obtained for a globe in regular use during a set of experiments and not to one which had been newly greased or otherwise altered from a previous condition :—

After 16 hours, weight = 3·53732 grams
,, 23 ,, = 3·53731 ,,
,, 40 ,, = 3·53726 ,,

or again,

After 17 hours, weight = 3·02086 grams
,, 23 ,, = 3·02084 ,,
,, 40 ,, = 3·02081 ,,

The first set of weights are those of a globe weighed full of gas at one atmosphere internal pressure ; the second set refer to the same globe weighed with gas at approximately 1 mm. pressure. Whether the globes were full or "empty," therefore, both sets of weighings showed a slight and regular decrease which was characteristic of every such weighing. In general, a further appreciable decrease was not observed; for example, the following figures represent weighings of one globe carried out on four consecutive days:—

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[*] 'J. Amer. Chem. Soc.,' vol. 22, p. 144 (1900).

First day	3·45333 grams.
Second day	3·45328 „
Third day	3·45327 „
Fourth day	3·45325 „

When, therefore, the characteristic drop of 0·04 to 0·06 milligram was obtained in the second day's weighings, further weighing was not carried out. Corresponding weights were employed in the density calculations.

The only difference between a globe and its counterpoise lies in the existence of the tap grease; it is probable that the above decrease in weight is due to progressive drying of the grease previously moistened by contact with ice and then exposed to the dry air of the drying-cupboard. It must be emphasized that such regular variation in weight was not at once observed after the regreasing of a globe tap. Large variations may then occur to begin with, a decrease of as much as 0·3 milligram per day being observed on one occasion. On the other hand, an increase in weight may be here experienced, due perhaps to oxidation of the grease exposed to the air. Obviously, then, the greasing of a tap is an operation to which great attention must be paid. Excess grease must not be used, and all exposed grease at the junction of tap-key and barrel completely removed. It was found best to suspend, finally, the globe in the drying cupboard for a week or more before actual experiments were resumed.

For the purpose of the density calculations, the average of the "weights empty" before and after a "filling" was taken as the weight to be subtracted from the weight of the full globe. While such "zero" weights showed occasionally irregular variation, the difference was generally small and, as before, frequently fairly regular, *e.g.*, 2·92637, 2·92641, 2·92647, 2·92650 grms. Such an increase is probably to be attributed to some progressive change in the condition of the tap grease.

Density Results.

The normal density is defined as the weight of the normal litre, *i.e.*, the weight of 1 litre of gas, at 0° C., at a pressure of 760 mm. of mercury, at sea-level and latitude 45° ($g = 980·616$).

The experiments gave (1) the weight of water at 0° C. required to fill the globe at 0° C., weighed with a certain set of weights, under the value of g for the laboratory; (2) the weight of phosphine gas at 0° C. required to fill the same globe at 0° C., at a certain known pressure, the gas being weighed with the same set of weights under the same value of g for the laboratory. The ratio of the weight of gas to the weight of water occupying the same volume under the standard conditions being known, the density of the gas can at once be calculated. The value of g for the laboratory need only be introduced in the reduction to standard conditions of the observed height of the mercury barometric column.

If W = weight of water, w = weight of gas, P_0 = (reduced) pressure in millimetres, d = density of water under standard conditions in grams per millilitre, and L = density of the gas at the measured pressure, corrected to 760 mm., then

$$L = (wd760/WP_0) \times 1000.$$

The factor W/d is usually designated as the "volume" of the globe. If P be exactly 760 mm., then $L = L_N$ represents the normal density. If P_0 be not exactly 760 mm., but have a value close to 760 mm., then L_N can be calculated from L by means of an approximate knowledge of the coefficient of compressibility.

The actual density at one-half atmosphere, say, is given by

$$L = (wd380/WP_0) \times 1000,$$

where P_0 is a pressure very close to 380 mm. As indicated earlier, for purposes of compressibility, these actual densities were converted to densities "per unit pressure"; in otber words, referred to the standard 760 mm. as if the gas laws were accurately obeyed. The difference from the normal density gives the divergence from the gas laws over the range of pressure considered. These densities per unit pressure are denoted by $L_{\frac{3}{4}}$, $L_{\frac{1}{2}}$ and $L_{\frac{1}{4}}$.

The following figures were employed in the calculations :—

Density of water under standard conditions = 0·999868 grams per millimetre.

Normal acceleration due to gravity = g_n = 980·616.

Laboratory acceleration due to gravity = g_l = 981·53 (calculated by the formula given by Germann, 'J. Phys. Chem.,' vol. 19, p. 471 (1915)).

Coefficient of cubical expansion of mercury = 0·0001818.

Coefficient of linear expansion of brass = 0·0000189.

The corrections applied in a calculation were as follows :—

(1) Correction for the buoyancy of the air on the weights.

(2) Correction for residual gas in the "empty" globe. The normal density of phosphine at very low pressures was here taken as 1·517 (results later).

(3) Correction for the contraction of the globe on evacuation.

(4) Correction for the cathetometer scale.

(5) Correction for the temperature of the mercury.

(6) Correction for gravity.

(7) Correction for compressibility. This correction was always small, being given by

$$A = A_0' (760 \cdot 00 - P_0)/760 \cdot 00,$$

A_0' was taken as 0·0090 (*cf.* later).

The following tables give the results obtained for the densities at the various pressures. P_0 is the fully corrected pressure, G the actual weight of gas in grams, while the final column gives the calculated value of L, the density per unit pressure.

Experiments.	Globe.	P_0.	G.	L.
1	I II	758·27 758·27	0·51258 0·52133	L_N = 1·5311(1) 1·5308(1)
2	I	764·10	0·51648	1·5308(0)
3	II	760·03	0·52247	1·5307(4)
4	I II	762·02 762·02	0·51504 0·52383	1·5307(3) 1·5305(4)
5	I II	761·86 761·86	0·51490 0·52374	1·5307(1) 1·5307(3)
6	I II	760·86 760·86	0·51422 0·52307	1·5307(7) 1·5308(0)
7	I	761·58	0·52250	1·5305(7)

Average L_N = 1·5307(2).

The figures of series 1 were obtained in the first experiment actually performed. Although the result by globe II is in good agreement with the results following, the result of globe I is distinctly high and was therefore rejected in the calculation of the average value. The cause would seem to be incomplete removal of moisture, either from the globe itself in the first instance, though this seems unlikely (see above), or from the rubber joint used to attach the globe to the apparatus. With reference to the former suggestion, it is not unusual for the first result of such a series of density determinations to be high.*

Three-quarters Atmosphere.

Experiments.	Globe.	P_0.	G.	L.
1	I	570·30	0·38458	$L_{\frac{3}{4}}$ = 1·5273(9)
	II	570·30	0·39116	1·5272(4)
2	II	569·48	0·39063	1·5273(2)
3	I	569·97	0·38428	1·5271(0)
	II	569·97	0·39092	1·5271(7)

Average $L_{\frac{3}{4}}$ = 1·5272(4)

One-half Atmosphere.

Experiments.	Globe.	P_0.	G.	L.
1	I	378·76	0·25487	$L_{\frac{1}{2}}$ = 1·5240(5)
	II	378·76	0·25919	1·5237(2)
2	I	378·80	0·25494	1·5242(3)
3	I	381·88	0·25690	1·5237(0)
	II	381·88	0·26132	1·5235(7)
4	I	379·99	0·25555	1·5232(6)
	II	379·99	0·26003	1·5237(6)
5	I	379·26	0·25514	1·5237(5)
	II	379·26	0·25953	1·5237(5)

Average $L_{\frac{1}{2}}$ = 1·5237(6)

One-quarter Atmosphere.

Experiments.	Globe.	P_0.	G.	L.
1	I	189·00	0·12696	$L_{\frac{1}{4}}$ = 1·5203(8)
	II	189·00	0·12903	1·5201(9)
2	I	188·52	0·12653	1·5202(2)
	II	188·52	0·12871	1·5203(2)
3	II	189·72	0·12951	1·5200(6)
4	I	189·94	0·12750	1·5204(7)
	II	189·94	0·12970	1·5204(7)

Average $L_{\frac{1}{4}}$ = 1·5203(1)

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* Guye, 'C. R.,' vol. 143, p. 1233 (1906); Gray and Burt, 'J. Chem. Soc.,' vol. 95, p. 1641 (1909).

The "probable error" of the mean has been calculated in the usual way from the above columns of figures. The density results can then be summarized as follows :—

$$L_N = 1{\cdot}5307\ (2) \pm 0{\cdot}0000\ (5)$$
$$L_{\frac{3}{4}} = 1{\cdot}5272\ (4) \pm 0{\cdot}0000\ (4)$$
$$L_{\frac{1}{2}} = 1{\cdot}5237\ (6) \pm 0{\cdot}0001\ (2)$$
$$L_{\frac{1}{4}} = 1{\cdot}5203\ (1) \pm 0{\cdot}0000\ (5).$$

Calculation of $(1 + \lambda)$.

Since the density is inversely proportional to the volume, relative values of pv for the corresponding pressures are obtained by dividing L_N, the normal density, by the density "per unit pressure." The value of pv at one atmosphere is here taken as unity. The values so obtained increase as the pressure decreases ; the problem is to determine the value of pv at zero pressure. The last column of the table below gives the increase of pv per atmosphere calculated for the corresponding pressure-ranges of three-quarters, one-half, and one-quarter atmosphere. The pressure in atmospheres is denoted by P.

P.	L.	pv.	$\Delta(pv)/\Delta p$.
1·00000	L = 1·5307(2)	1·00000	—
0·75000	1·5272(4)	1·0022(8)	0·0091(12)
0·50000	1·5237(6)	1·0045(7)	0·0091(34)
0·25000	1·5203(1)	1·0068(5)	0·0091(32)

It appears from the figures of the last column that the relationship between pv and p is linear with respect to p. The average value of 0·0091 (25) is therefore adopted for $\Delta(pv)/\Delta p$. The factor $(1 + \lambda)$ for phosphine gas is then represented by the number 1·0091 (2).

The Molar Weight of Phosphine and the Atomic Weight of Phosphorus.

If L represent the weight of the normal litre of phosphine, L_0 that of the normal litre of oxygen, and $(1 + \lambda)$ and $(1 + \lambda_0)$ refer to the corresponding compressibilities, then the molar weight of phosphine gas, on the basis $O = 16$, is given by

$$M = L\,(1 + \lambda_0)/L_0\,(1 + \lambda)\ 32$$

Taking then

$$L = 1{\cdot}5307\ (2),$$
$$L_0 = 1{\cdot}4290\ (0),$$
$$(1 + \lambda) = 1{\cdot}0091\ (2),$$

and

$$(1 + \lambda_0) = 1 \cdot 0009\ (6),$$

the molar weight of phosphine is calculated to be 34·000, and the atomic weight of phosphorus 30·977.

Discussion.

The question of adsorption of gas on the walls of the density globe is one which is very difficult to investigate experimentally. Until recently, it has been generally assumed* that the gas film at 760 mm. pressure is sensibly the same as the gas film at 1 mm. pressure, an assumption which would appear to be justified in the case of the permanent gases. The standard gas oxygen is itself a permanent gas, and if any error through this cause does occur, practically the same error will be experienced in the case of any other permanent gas, so that both density and compressibility can be regarded as in error by very nearly the same amounts respectively in the two cases. The results for molar and atomic weights should, therefore, on this account at least, show good agreement with the results obtained by other methods. In the case of the more easily condensable gases, however, such as phosphine, hydrochloric acid gas, sulphur dioxide and the like, the error arising in this way may be expected to be correspondingly greater. The normal density, calculated on the assumption that the gas films are equal for the two extremes of pressure, will be too large.

It is usually considered advisable that such density determinations be carried out with density globes that differ considerably in volume and therefore in surface exposed to the gas.† If such be the case, the smaller globe will give the higher density, since the surface per unit volume will be greater; in general, however, an examination of density results yields no definite information on this matter, such variation being apparently overshadowed by the errors involved in the experimental manipulation. Again, the time given for the establishment of a new equilibrium in gas-film for a new pressure must be considered. In any case, such an adsorption correction for phosphine is not likely to be greater than the corresponding correction for a gas such as carbon dioxide, which is given by Moles‡ as of the same magnitude as that of oxygen While the possibility of such an error due to adsorption must be admitted, it would appear probable that, for phosphine gas, the error involved is for these purposes negligible.

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* *Cf.*, however, Gray and Burt, *loc. cit.*

† *Cf.* Moles, ‘Ber. D. Chem. Ges.,’ vol. 59, p. 740 (1926); Scheuer, ‘Z. Phys. Chem.,’ vol. 68, p. 577 (1909).

‡ ‘Rec. Trav. Chim. Pays-Bas,’ vol. 48, p. 866 (1929).

In the case of phosphine, that part of the experimental work which would appear to be of the greatest importance is the purification of the gas by fractional distillation. It has been already remarked that rapid distillation at room temperature was accompanied by production of traces of hydrogen gas, and that no matter how many such distillations were given the purity of the resulting product could not be considered to be improved. It is therefore to be expected that the figure for the normal density would, on this account, be low. It appears probable that Gazarian's result of 1·5293* is low for this reason, as is suggested by Baxter and Jones.† The most probable value for the normal density of phosphine gas, from the experiments here described, is not less than 1·5307.

In the case of the compressibility, the factor $(1 + \lambda)$ would not be affected by any small percentage of impurity, assuming such impurity to be of constant proportion in all the density determinations. From the adsorption point of view, the density results at one-quarter atmosphere would be more accurate than those at the higher pressure of one atmosphere. The compressibility factor would accordingly tend to be too large. The figure actually obtained for $(1 + \lambda)$ for phosphine in these experiments is 1·0091 (2), on the assumption, borne out by the data, that the curve representing the variation of pv with p is a straight line. If the gas-laws are accurately obeyed at zero pressure, $\Delta(pv)/\Delta p$ will be zero. It is possible, of course, that such a zero coefficient will not make its appearance until the pressure is exceedingly low. In any case, the value for $(1 + \lambda)$ will again be too large. For these reasons, the most probable value for $(1 + \lambda)$ would appear to be not greater than 1·0091.

The final figure obtained for the atomic weight of phosphorus in this investigation is 30·977,‡ which represents a difference of 1 in 6000 from the value 30·982 obtained by Aston. The application of the foregoing considerations would in every case tend to decrease this divergence.

Summary and Conclusions.

Determinations of the density of phosphine gas were carried out at the pressures of one atmosphere, three-quarters atmosphere, one-half atmosphere, and one-quarter atmosphere. The gas was prepared by the action of dilute potassium hydroxide solution on solid phosphonium iodide and purified by fractional distillation. The value for the normal density thus obtained was

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* 'J. Chim. Phys.,' vol. 7, p. 341 (1909).

† 'J. Amer. Chem. Soc.,' vol. 32, p. 298 (1910).

‡ Values of 30·97 (9) and 30·98 (2) were given in a preliminary note in 'Nature,' vol. 123, p. 838 (1929).

$$L_N = 1 \cdot 5307,$$

and the factor for compressibility between zero and one atmosphere pressure was found to be $(1 + \lambda) = 1 \cdot 0091$. The molar weight of phosphine is then calculated to be 34·000 and the atomic weight of phosphorus 30·977.

The estimated accuracy is of the order of 1 in 10,000.

The author desires to express his indebtedness to Sir James Walker and Dr. S. A. Kay for the valuable advice and the kind interest shown during this investigation, to Mr. Walter Murray, A.I.C., for his able assistance and advice in many practical problems, and to Imperial Chemical Industries, Ltd., for a grant which permitted the purchase of certain apparatus.

The Spectrum of H_2 : *The Bands Ending on* $2p\,{}^1\Pi$.

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(Communicated by O. W. Richardson, F.R.S.—Received May 31, 1930.)

In a recent communication* a new system of bands in the molecular spectrum of hydrogen has been outlined. These bands were found to originate in known par-hydrogen levels having principal quantum numbers 3 and 4, and to go down to the $2p\,{}^1\Pi$ or C level of Dieke and Hopfield. The present paper is an extension of the original, and also deals with some apparent anomalies in the rotational structure of the $2p\,{}^1\Pi$ levels for the vibrational states corresponding to $v'' = 1$, 2 and 3. These new bands were derived from the old bands to the $2p\,{}^1\Sigma$ or B state, together with the required infra-red interval between the $2p\,{}^1\Sigma$ and $2p\,{}^1\Pi$ states, as determined from the existing ultra-violet data on transitions from these two states to the $1s\,{}^1\Sigma$ or A state of the molecule.

Bands were found corresponding to transitions from $3\,{}^1A$, $3\,{}^1C$, $3\,{}^1K$, $3\,{}^1O$, $4\,{}^1A$, $4\,{}^1B$, $4\,{}^1C$, $4\,{}^1E$ and $4\,{}^1\chi$ to $2p\,{}^1\Pi$. Since the A, B and C states with principal quantum numbers 3 and 4 are thought to be similar in nature, bands were expected for $3\,{}^1\mathrm{B} \rightarrow 2p\,{}^1\Pi$ transitions. These were not found in the original analysis, but in the present investigation, using Poetker's* tables of infra-red lines together with those of Gale, Monk and Lee,† these bands have been identified both for the $0' \rightarrow 0''$ and $1' \rightarrow 1''$ vibration transitions. The presence of these bands, together with the relative positions and corresponding behaviour of the branches of the A, B and C bands in the (ν, m) diagram for both systems, are in strong support of the above assumption regarding the common nature of these states for both electronic levels. This point has already been discussed by Richardson in connection with the structure of their rotation levels.

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* Richardson, 'Roy. Soc. Proc.,' A, vol. 126, p. 487 (1930).

These $3\,{}^1\mathrm{B} \rightarrow 2p\,{}^1\Pi$ lines are given in Table I. It may be recalled that in the case of the $4\,{}^1\mathrm{B} \rightarrow 2p\,{}^1\Pi$ band, the Q lines are very much stronger than the P lines, so that the absence of the P lines is not surprising in the present case where even the Q lines are extremely faint.

Table I.

$3\,{}^1\mathrm{B} \rightarrow 2p\,{}^1\Pi$ lines.

The $0' \rightarrow 0''$ band.		$1' \rightarrow 1''$	
Q 2	12920·57 (1) P	Q (2)	12714·6 (1) P
Q 3	*a*	R (2)	12796·6 (3)
Q 4	12812·32 (1) P	P (4)	12509·7 (1)
Q 5	12746·27 (0) P		
P 4	12694·2 (1)		

In the case of the $1' \rightarrow 1''$ lines R (2) seems much too strong, and P (4) is hardly to be expected all alone. It may be that the strength of these lines is due to superposed lines of unidentified systems of bands. Q (2) seems likely to be correct as its intensity is of the order expected.

In connection with the re-determination of the rotation levels for the states given by $n'' = 1$, 2 and 3, it should be noted that for $n'' = 1$, the values of ε as originally found were about equal but opposite in sign for the (P, R) and Q levels. Moreover, the value of ε changed abruptly for the Q levels from $-\frac{1}{2}$ for $n'' = 0$ to $+\frac{1}{2}$ for $n'' = 1$ and remained positive for $n'' = 2$ and 3. In the case of the (R, P) levels for $n'' = 2$ two alternative values were given for $\mathrm{F}''(4) - \mathrm{F}''(3)$.

Because of this added element of doubt, a complete re-determination of the $2' \rightarrow 2''$ bands was carried out. This led to the introduction of a number of new lines in place of those previously listed, and also to the classification of others belonging to rotational levels with higher m-values than those hitherto determined. There is a slight possibility that the P (5) lines should all be missing, and the R (5) lines of $3\,^1A$ and $3\,^1C$ put in instead. The determination of both P (5) and R (5) lines involves the same infra-red interval; but as different intervals are required to give these two sets of lines, one set must be discarded. Since in general there are more R lines than P, the R (5) lines should, perhaps, be included, but in view of the larger number of P (5) lines supporting the P (5) interval, and the fact that this interval is more nearly equal to the average obtained from the ultra-violet data, these have been used in calculating the rotational levels for the $n'' = 2$ state. Moreover, if the R (5) lines are used instead, $F''(5) - F''(4)$ becomes 237·8 instead of 232·7 with a resulting $\Delta_2\nu = 76{\cdot}9$ and $\Delta_3\nu = 18{\cdot}9$. These successive differences are thought to be less probable than those arising from the P (5) lines and set forth in Table III.

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* Poetker, 'Phys. Rev.,' vol. 30, p. 418 (1927).

† Gale, Monk and Lee, 'Astrophys. Journal,' vol. 67, p. 89 (1928).

Using the approximate formula $F(m) = B_n (m + \varepsilon)^2$ for small values of m, together with the value of B_n determined from the rotational data, the values of ε were found to be $-0{\cdot}505$ and $-0{\cdot}726$ for the Q and (P, R) levels respectively. The higher value in the case of the (P, R) levels may be accounted for by the marked increase in the second rotational difference with increasing m-values. Had any $m'' = 1$ lines been present the value of B_n would probably have been lower, thus indicating that the values of B_n and ε should be approximately equal for the (P, R) and Q states, as found for $n'' = 0$. On the other hand, it is possible that the R (2) lines are wrong, as pointed out later.

The essential agreement between the $n'' = 0$ and $n'' = 2$ states at once led to the question as to whether the molecular constants of the $n'' = 1$ state could be correct. A redetermination of these lines led to practically the same results for the (P, R) levels as had previously been obtained, with only one or two minor changes. In the case of the Q levels considerable difficulty arose due to the scarcity of Q (3) lines. No check for different Q (3) lines could be obtained within reasonable limits of the average infra-red interval, so that a (ν, m) graph was made for the Q branch of ($1' \rightarrow 1''$), $3\,^1C \rightarrow 2p\,^1\Pi$ which gave the position of Q (3) for this band as 12475·8. As this is the strongest band, one expects this line to be present, and since it is only 2·2 ν from the calculated position based on ultra-violet data alone, it is almost certain to be the correct line. Using this to re-calculate the Q rotation levels in the usual way the values of B_n and hence of ε were determined. For the Q-states ε now becomes $-0{\cdot}543$ and for the (P, R) states $-0{\cdot}481$. The rotational levels for this state are included in Table III, and all the lines for the $1' \rightarrow 1''$, $2' \rightarrow 2''$ and $3' \rightarrow 3''$ bands are given in Table II.

Table II.

$1' \rightarrow 1''$.

Initial state.	3 ^{1}A.	3 ^{1}B.	3 ^{1}C.	3 ^{1}K.	3 ^{1}O.
Q 2	*a*	12714·6 (1) P	12574·6 (0)	12423·10 (0)	13840·6 (00*b*)
Q 3	*a*	*a*	?12475·8 (1)	*a*	*a*
Q 4	*a*	*a*	12350·3 (0)	*i*	13801·7 (1*a*)
Q 5	*a*	—	?12214·0 (0) P	—	—
Q 6	—	—	?12068·1 (1) P	—	—
P 2	—	—	12586·8 (1*b*)	12403·9 (00)	—
P 3	12649·1 (0*a*)	*a*	*a*	*i*	13721·9 (0)
P 4	*a*	12509·7 (1)	12295·6† (3)	12169·8 (0)	*a*
P 5	*a*	*a*	12122·5 (1)	12016·5 (00*a*)	*a*
R 2	12896·2 (00)	12796·6 (3)	12588·8 (00)	*a*	13937·2† (2)
R 3	12927·6 (1*a*)	*a*	12518·7 (1)	*i*	*a*
R 4	*a*	*a*	*a*	12335·9† (1)	*a*
R 5	—	*a*	—	?12350·3 (0)	—

$2' \rightarrow 2''$.

Initial state.	3 ^{1}A.	3 ^{1}C.	3 ^{1}K.	3 ^{1}O.
Q 2	*a*	12403·9 (00)	12475·8 (1)	13710·7 (1)
Q 3	12612·5 (00)	*a*	12411·9† (2)	—
Q 4	12595·3 (1)	*a*	12314·8 (1) P	13690·8 (0)
Q 5	12561·5 (0)	*a*	12191·5 (0) P	—
P 2	*a*	*a*	*a*	*a*
P 3	12495·4 (00)	*a*	12365·2 (1)	13600·4 (4)
P 4	*a*	*a*	*a*	—
P 5	12363·1 (0)	11956·8 (0) P	12082·2 (1) P	13458·2 (0)
R 2	12713·5 (00)	12411·8† (2)	*a*	14097·33† (0)
R 3	12756·6 (0)	12350·3 (0)	12475·8 (0)	13851·8 (00)
R 4	12775·9 (0) P	12252·2 (0)	*a*	—
R 5	*a*	*a*	—	—

$3' \rightarrow 3''$.

Initial state.	3 ^{1}A.	3 ^{1}C.
Q 2	*a*	?12179·3 (00*a*)
Q 3	*a*	*a*
Q 4	*a*	?11993·90 (00)
Q 5	—	—
P 2	—	—
P 3	*a*	12063·7 (00)
P 4	*a*	*a*
P 5	—	—
R 2	*a*	?12193·2 (0) P
R 3	12355·6 (2*bd*) P	12135·9 (1*h*)
R 4	*a*	?12046·7 (0) P
R 5	—	—

There are two alternative possibilities, besides that given in Table II, for Q (5) lines of the 1′ → 1″ bands, viz., 12713·5 (00) for 3 ¹A and 12122·5† (1) for 3 ¹K, or 12205·3 (0) for 3 ¹C and 12112·0 (0) for 3 ¹K. The former seems unlikely as there are no other Q lines for 3 ¹A, and the 3 ¹K line is already assigned to P (5) of 3 ¹C. The latter may be correct, but this value of Q (5) for 3 ¹C seems out of place if Q (6) is anywhere near being correct, and there is no reason to expect Q (5) of 3 ¹K since Q (3) is missing. The value 12214·0 (0) P was therefore taken as being the best Q (5) line based on the ultra-violet data and also fitting in with the approximate Q (6) position obtained in the same way.

Since 3′ → 3″ lines were found only for 3 ¹A and 3 ¹C an attempt was made to check the 3″ rotation levels. Assuming the averages of the infra-red intervals to be correct to within 1·5 ν, possible lines were found for 3 ¹C; and one R (3) line checked accurately with R (3) and P (3) of 3 ¹C. Using these lines a rough estimate was obtained for the 3″ levels as given in Table III. This led to a value of 2B*n* = 54·13 and ε = − 0·58 for the (P, R) states, but due to the absence of any Q (3) lines the Q constants could not be determined. Using the calculated position of the Q (3) line of 3 ¹C, however, ε = − 0·474, thus indicating that the sign of ε remains constant for all the vibration states.

Table III.

	j ↓	*n*″ → 1		2		3	
P, R	5						
		220·46		232·7			
	4		44·91		71·8		
		175·55		160·9		157·25	
	3		58·17		58·0		54·13
		117·38		102·9		103·12	
	2						
	2B	58·17		58·0		54·13	
	ε	−0·481		−0·726		−0·58	
Q	6						
		?284·22					
	5		61·26				
		222·96		214·1			
	4		50·23		51·1		
		172·73		163·0			
	3		58·42		54·43	257·59	
		114·31		108·57			
	2						
	2B	58·42		54·43		50·85	calc.
	ε	−0·543		−0·505		−0·474	calc.

Rotation Levels of $2p\,^1\Pi$.

In the $1' \rightarrow 1''$ bands the $F''(3) - F''(2)$ rotation difference was checked by a P (2) line of $3\,^1K$ which might have been chosen instead of P (2) of $3\,^1A$. This gave 117·03 for the interval, this value being 0·35 ν lower than that derived from the R lines. The infra-red interval indicated by the R (3) lines was used to give the P (3) lines listed in Table II. The P (4) lines have been changed from those given by Richardson. The new, slightly changed interval allows for two P (4) lines, viz., for $3\,^1C$ and $3\,^1K$ instead of one for $3\,^1C$ only as previously stated. This may or may not be an improvement, but as P (2) exists for $3\,^1K$, P (4) is likely to occur as well. With the P (4) lines changed, the new infra-red interval leads to an R (4) line for $3\,^1K$; but this line is already claimed by another band, and its presence as an R (4) line in the present band system may therefore be fortuitous.

It is thought that the changes which have been made in the lines of the axial bands are fully justified. Though certain alternative possibilities have been put forward, the opinion of the writer is that the data included in Tables II and III carry more weight than any of the alternatives. Moreover, during the progress of the work graphs of the (ν, m) relation were made for all bands, and the form of the bands was found reasonable wherever a sufficient number of lines was present to determine the shape of the curves.

In the tables those lines which depend on ultra-violet data alone are marked by an interrogation point. A dagger denotes the fact that the line is shared by other bands, *i* that the line may be present but masked by nearby stronger lines,—that the position of the line is unknown, and *a* that the position has been calculated and the line is absent. The lines marked P are Poetker's lines, but are 0·4 ν lower than the values which he records. This seems to be the approximate average discrepancy between his values and those of Gale, Monk and Lee. Actually the differences vary irregularly between 0 and 0·5 ν.

Calculations were made for the $m = 2$, 3 and 4 lines of all bands involving initial and final vibration quantum numbers from 0 to 3. The lines which were found are listed in Table IV.

It should be noted in this connection that all $0' \rightarrow 3''$ and $1' \rightarrow 3''$ lines for bands arising from states with principal quantum number 3, and also those of $0' \rightarrow 2''$ for $3\,^1A$, $3\,^1C$, $3\,^1K$ and $3\,^1O$ are beyond the red limit of the tables, both of Poetker and of Gale, Monk and Lee. A few lines have been recorded for bands arising from $3\,^1L$, $3\,^1N$, $3\,^1M$ and ^1Q; but it is thought that, though the lines found agree with the calculated positions to the required accuracy,

Table IV.

Lines off the axis—

$0' \rightarrow 1''$	$3\,^1$O : R (2) 11676·8 (00*a*) ; $3\,^1$N : Q (2) 13680·4 (1), Q (4) 13566·9 (00) ;
	$4\,^1$E : R (4) 15817·47† (3). Q (2) 15927·8† (1).
$0' \rightarrow 2''$	$4\,^1$A : P (4) 13937·24† (2) ; $4\,^1$E : R (3) 13715·7 (3).
$0' \rightarrow 3''$	$4\,^1\chi$: R (2) 12072·5 (1*h*) P.
$1' \rightarrow 0''$	$3\,^1$N : Q (2) 17955·6 (1), Q (4) 17778·92 (4) ; $3\,^1$M : Q (2) 16426·79 (1) ;
	^{1}Q : P (3) 12850·28 (1*h*) P.
$1' \rightarrow 2''$	$3\,^1$N : P (5) 13100·08 (2) P.
$1' \rightarrow 3''$	———
$2' \rightarrow 0''$	$3\,^1$C : R (2) 16895·24 (0), Q (3) 16774·97† (4) ; $3\,^1$K : R (4) 16745·48 (0) ;
	$3\,^1$O : Q (2) 18187·92 (1*h*) ; $3\,^1$L : P (4) 17494·35† (1).
$2' \rightarrow 1''$	———
$2' \rightarrow 3''$	———
$3' \rightarrow 0''$	$3\,^1$C : R (4) 18527·75 (0).
$3' \rightarrow 1''$	$3\,^1$A : Q (2) 16484·00 (1) ; $3\,^1$C : R (2) 16416·35 (2), Q (3) *i*.
$3' \rightarrow 2''$	$3\,^1$C : Q (2) 14219·5 (00), R (3) 14181·3† (3).

Other odd lines $1' \rightarrow 1''$ $4\,^1\psi$: R (2) 18311·28 (2) ; $3\,^1$N : Q (2) 15650·27† (1).
λ 4097 progression : R (2) 13261·9 (3), Q (5) 13195·45 (2) P, P (4) 12975·0 (1*a*), P (5) 13148·3†(4).

their presence is very likely fortuitous as there are no lines occurring for the $0' \rightarrow 0''$, $1' \rightarrow 1''$ or $2' \rightarrow 2''$ bands arising from these levels. In the case of $3\,^1$N, however, the lines seem more likely to be correct than for the others, as the Q 2 and Q 4 lines occur for both the $0' \rightarrow 1''$ and the $1' \leftarrow 0''$ transitions, and Q (2) of $1' \rightarrow 1''$ may also be present but masked by the line 15650·27 (1) which differs by 0·3 ν from the calculated position. In general the lines found involve only low rotational numbers, as one would expect from the weakness of the axial bands.

No lines for the $2p\,^1\Pi$ bands were found using the old $0''$ band belonging to the λ 4907 progression, but the $1''$ band led to four possible lines, viz., R 2, P (4), P (5), and Q (5). Since P (2) and P (3) are not derivable, there being no Q lines in the original band with m less than 3, these lines are included under the heading of odd lines in Table IV. As they exist only for the $1''$ band, it is assumed that they must belong to a $1'$ progression, and hence that the bands to the $2p\,^1\Sigma$ state also form a $1'$ progression.

Throughout the paper only those lines have been included whose wave-numbers agreed with the calculated values to within 0·2 ν. The average infra-red intervals as calculated from the ultra-violet data of Hyman (unpublished), Hori, Schlaafsma and Dieke, are all within 2·0 ν of the values finally employed except in the case of that used to determine the R (2) and P (2) lines of $1' \rightarrow 1''$ band. Here the discrepancy was 6 ν, but the ultra-violet data were rather scarce in this case, and as there are six satisfactory lines obtained which give reasonable values for 2B and ε for the $1''$ state of $2p\,^1\Pi$, it is thought that the error must lie in the ultra-violet classification. In the case of the R (2) lines of the $2' \rightarrow 2''$ bands, the calculated infra-red interval seemed correct to within

1·1 ν; but as there is only one R (2) line in these bands which is not already claimed by another band, there may be a slight error here which could account for the abnormally large value of ε in the case of the (P, R) levels of the 2″ state in $2p\,{}^1\Pi$. With the data available at present it is impossible to offer any explanation of the sudden increase in the second rotational difference in this level. It is thought that the accuracy throughout is as great as can be attained, and that the general rotational structure of the $2p\,{}^1\Pi$ state is correct.

Richardson and Davidson* published a series of bands arising from states with total quantum number 4 and ending on $2p\,{}^1\Sigma$ levels. In the case of the $4\,{}^1\chi - 2p\,{}^1\Sigma$ bands two alternative R (2) progressions have been inserted. In discussing these Richardson places the progression beginning with 27510·53 (00) F as being the correct one to associate with this band because in the 0′ → 0″ band of $4^1\,\chi - 2p\,{}^1\Pi$ this line gives rise to a Q (3) line whereas the other does not. Since Q (4) and Q (5) lines are derivable from the R (3) and R (4) lines of the old bands, this appears to be in strong support of this progression. However, the adoption of this, in place of the second progression beginning with 27651·03 (0/1) F, leads to extreme abnormalities in the rotational structure of the $4\,{}^1\chi$ vibration states, which seem very improbable. The rotational structure for the two cases is shown in Table V.

Table V.

Alternative Rotational Structures for $4\,{}^1\chi$, $n' = 0$.

j				
6	———		———	
	169·95		169·95	
5	………	68·26	………	68·26
	101·69		101·69	
4	———	70·26	———	19·76
	31·43		81·93	
3	………		………	
	R (2) = 27561·03		R (2) = 27510·53	

The irregular behaviour of the band in the second case is even more plainly seen from the (ν, m) plot, as it is impossible even to approximate to a simple curve through the four points, whereas the former will give an approximate parabola. Both progressions have points in their favour, but both are weak and found only in Finkelnburg's† tables, so that they may even be fortuitous.

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* ‘Roy. Soc. Proc.,’ A, vol. 123, p. 466 (1929).

† Finkelnburg, ‘Z. Physik,’ vol. 52, p. 26 (1928).

On the other hand the Q (3) line of the $4\,^1\chi \rightarrow 2p\,^1\Pi$ band may be there by chance, and if very weak it might actually exist for the alternative rotational structure of $4\,^1\chi$ and be masked by an α-band line of intensity 2 which is only 0·35 ν from the Q (3) position calculated on this basis.

The P (4) line of $4\,^1\chi \rightarrow 2p\,^1\Pi$ as calculated from R (2) = 27510·53 ($4\,^1\chi \rightarrow 2p\,^1\Sigma$ band) is claimed by another line, and as the R (2) line does not exist, the argument in support of this line is by no means complete.

In accordance with the new interpretation* of the $4\,^1\mathrm{B} \rightarrow 2p\,^1\Sigma$ lines as Q and S lines instead of R and P, the lines given by Richardson as P (3), P (4) and P (5) of $4\,^1\psi \rightarrow 2p\,^1\Pi$ ($1' \rightarrow 0''$) should be called R lines, if this $4\,^1\psi \rightarrow 2p\,^1\Sigma$ is considered to be the $1'$ progression of the former. If this is the case the $1' \rightarrow 1''$ lines should certainly be present for the band going to $2p\,^1\Sigma$, yet a renewed search led to no further lines for this band.

In conclusion I wish to express my gratitude to Prof. O. W. Richardson who suggested the problem and gave much helpful criticism throughout the progress of the work. I am also indebted to McGill University, Montreal, for a Moyse Travelling Scholarship which has made this research possible.

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* 'Roy. Soc. Proc.,' A, vol. 126, p. 487 (1930).

The Polar Properties of Single Crystals of Ice.

By John Mead Adams, Ph.D., Associate Professor of Physics in the University of California, Los Angeles.

(Communicated by H. Bateman, F.R.S.—Received May 9, 1930.)

[Plate 7.]

Although the crystallography of ice has been the subject of much study,* there is still no general agreement upon it. This is due chiefly to the fact that in the absence of authentic single crystals of ice with well-defined natural faces, the available material has been limited to specimens formed under uncontrolled and in most cases obviously complex conditions. The approach by way of the X-ray analysis of structure has now reached substantial conclusions in the work of Barnes,† and it remains to compare these conclusions with observations on single crystals of ice of simple forms, grown under controlled conditions.

Such crystals, of microscopic size, have now been made‡ and photographed, and the figures of Plate 7 reproduce some photographs of collections and individuals which seem most significant for the present study. The crystals were photographed as they lay on a glass plate which had been ruled with lines 0·01 cm. apart, thereby supplying the photographs with a linear scale. The optical system was similar to that of a microscope as ordinarily used, when the object is viewed by light from a source about 25 cm. distant, traversing the slide from below. Figs. 1 to 4 inclusive, which have been enlarged 55 diameters, show four successive stages in the growth of a collection of crystals. Most of the individuals are seen to pass through these stages with a proportional increase in all their dimensions, and without any perceptible change of shape—an observation which gives strong support to the view that they are monocrystalline.

Figs. 5 to 8 inclusive, enlarged 315 diameters, show individuals which are typical of the great majority of the simple forms observed. That in fig. 5 is obviously a plate or short column terminated by two basal planes, on one of which it is in contact with the glass, the line of view coinciding with the C axis.

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* Dobrowolski, ‘Arkiv Kemi. Min. Geol.,’ vol. 6, pp. 1–53 (1916), and many references there cited.

† ‘Roy. Soc. Proc.,’ A, vol. 125, p. 670 (1929).

‡ Adams, ‘Phys. Rev.,’ Series II, vol. 35, p. 113 (1930).

Measurements on many such crystals have failed to reveal any systematic departure from equality of the angles, and so far as this evidence goes the ice crystal is not limited to three planes of symmetry intersecting in the C axis. but may have even six such planes. The latter number is rendered improbable, however, by the complete absence of any twelve-sided prisms or pyramids. Fig. 6 is readily understood as the same shape as fig. 5, viewed at right angles to the C axis. It appears, therefore, that a right hexagonal prism, with the height nearly equal to the diameter of the base, is a frequently occurring shape for these small ice crystals. Whether all six columnar faces are present cannot be decided from fig. 6, but in fig. 7 an unequal development of the six faces reveals their presence. Fig. 8, on the other hand, indicates that the surface of the glass may often suppress three of them.

The examples thus far cited give no evidence of crystallographic polarity. The first observation bearing upon this matter is that of a decided tendency toward twinning on the basal plane. Fig. 9, enlarged 205 diameters, shows an excellent example in the lowest crystal of the central group, and the large crystal at the upper right of the group is almost equally striking. Comparison with figs. 10 (315 diameters) and 6 raises the question whether even some of the apparently simple hexagonal prisms may not be similarly composed. In the investigation of this question additional evidence of polarity came to light. A collection of crystals was exposed, at one stage of their growth, to a warm unsaturated atmosphere favourable to evaporation. Figs. 11, 12, 13 (300 diameters) show the history of one crystal of this collection. In fig. 11, it gave promise of developing like fig. 6. In fig. 12, at the onset of evaporation, two pits appeared at the ends of the C axis, and in fig. 13, after growth had been resumed, the appearance of fig. 6 was nearly restored. Fig. 14 (300 diameters), another crystal of the same collection, at the same stage as fig. 12, shows the end view of a similar pit. That these last two crystals overlie a ruling on the glass is immaterial; many others remote from a ruling show the effects almost as well. The cause of the formation of these pits may be sought in possible variation of thermal conductivity in different directions in the crystal, but that is aside from the present question. The significant fact is that while one crystal was developing these pits at the *ends* of its C axis, a similar one of the same collection, at the same three stages of growth, yielded figs. 15, 16, 17 (300 diameters) in which a cavity appeared and disappeared at the *middle* of the C axis. Fig. 16 indicates strongly that this cavity was associated with a twinning plane. Search was then made for crystals developing only *one* pit while undergoing evaporation, and in photographs of another collection under similar treatment the series consisting of figs. 18, 19, 20 (325 diameters) was found.

The crystal of figs. 18–20 thus displays a definite lack of symmetry, in structure, with respect to the (0001) plane, and supports the view that in the ice-crystal disintegration occurs more readily at one end of the C axis than at the other. This view, based on observations of natural snowflakes, has been advanced by Dobrowolski (*loc. cit.*) and others. He adduces the evidence of rod-shaped snowflakes, of which some are pointed only at one end, while others, terminated at both ends by basal planes, have the appearance of having grown from the union of two of the former, point to point. Mügge* cites examples of minerals which give evidence both of comparative instability at one end of a polar axis and of a tendency to twin on the corresponding basal plane. Johnsen,† from a study of numerous cases of soluble crystals, draws the conclusion that twinning, when it occurs in polar crystals, is determined by the difference in solubility at the ends of the polar axis. The crystal of figs. 15–17 is clearly an example of the tendency of ice to twin on the less stable basal plane, while the crystal of figs. 11–13 indicates that twinning may also occur, in ice, in the other mode, with the more stable ends of the polar axis joined. The strikingly different courses of development followed by these two crystals apparently similar at first, can hardly be explained otherwise.

The conclusion that the C axis in ice is a polar axis is not necessarily contradictory to the conclusion reached by Barnes (*loc. cit.*). The results of his X-ray analysis require that the (0001) plane shall be a plane of symmetry so far as the arrangement of oxygen ions in the lattice is concerned, but leave considerable room for conjecture as to the location of the hydrogen ions. It may well be that the asymmetric location of the hydrogen ions in a non-polar oxygen lattice confers the necessary polarity on the structure as a whole.

I am indebted to Mr. L. H. Humason for assistance in enlarging the photomicrographs.

Summary.

Photomicrographs of monocrystalline specimens of ice show some individuals which, though having the simple external form of a short right hexagonal prism terminated by basal planes, give evidence of polar structure. This evidence consists in the appearance of a pit at one end only of the C axis, when the

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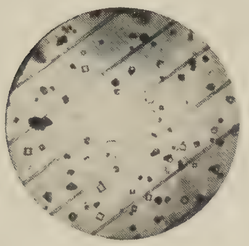
* ' Neu. Jahrb. Mineralogie,' vol. 16, p. 451 (1903).

† ' Neu. Jahrb. Mineralogie,' vol. 23, p. 339 (1907).



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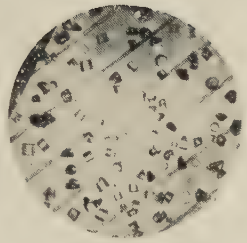

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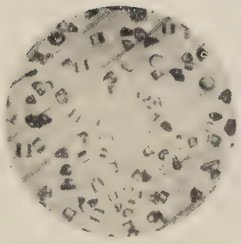

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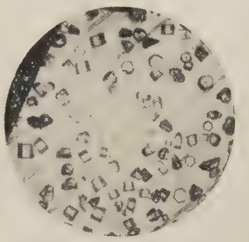

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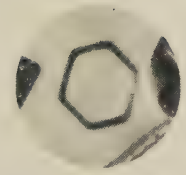

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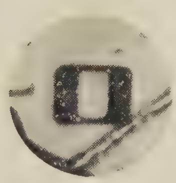

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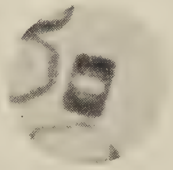

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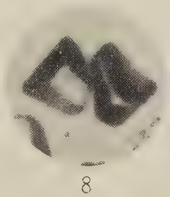

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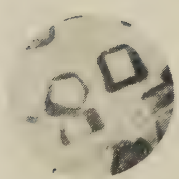

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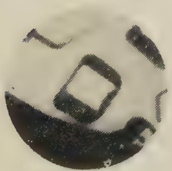

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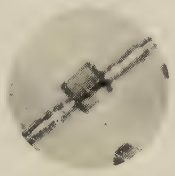

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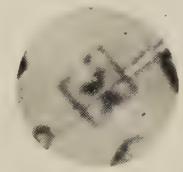

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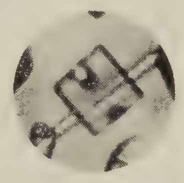

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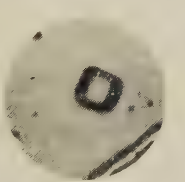

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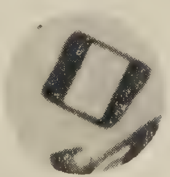

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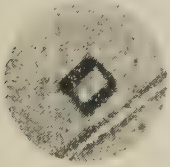

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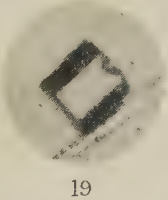

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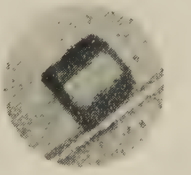

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crystal is brought into an atmosphere favourable to disintegration. Two other types of disintegration are observed in crystals of the same external form, one type characterised by a pit at each end of the C axis, the other by a cavity at the middle of the C axis. These two types are explained as due to the two possible modes of twinning of a polar crystal on the basal plane. In view of the conclusions of Barnes, the polarity of the ice crystal is ascribed to the asymmetric location of the hydrogen ions in the lattice with respect to the basal plane.

The Intensity of Quadripole Radiation in the Alkalis and the Occurrence of Forbidden Lines.

By A. F. Stevenson, University of Toronto.

(Communicated by R. H. Fowler, F.R.S.—Received May 30, 1930.)

1. The occurrence of the series 1S — *m*D in the spectra of the alkali metals, in particular the line 1S — 3D, has been observed, both in emission and absorption, by several authors,[*] although such transitions are forbidden by the selection rule for azimuthal quantum numbers. Such lines are very weak, and might be caused by the presence of ionic or other external electric fields, in which case the selection rule may be violated; but they have been observed in emission under conditions which were thought to preclude the existence of such fields, and certainly this would be the case in absorption. Another explanation must therefore be sought.

It is now recognised that the ordinary formula for the intensity of a spectral line as given by quantum mechanics, and which yields the selection rules, is only a first approximation, which amounts to taking the " dipole moment " of the atom. A more exact treatment yields higher order terms as corrections, and these so-called " multipole " terms, though much weaker than the ordinary dipole ones, may allow transitions which are " forbidden " by the ordinary selection rules. In this paper, the absorption intensities of the line 1S — 3D for the alkalis, lithium, sodium, potassium and rubidium, are calculated on the supposition that this line is due to " quadripole " radiation, using Hartree's method of self-consistent fields for the radial wave-functions, and it will be seen that the calculated intensities agree fairly well with the observed, where such are available, considering the uncertainty in the experimental result. A similar explanation has been given in support of Bowen's hypothesis regarding the occurrence of certain nebular lines.[*]

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[*] Sowerby and Barratt, 'Roy. Soc. Proc.,' A, vol. 110, p. 190 (1926); Schrum, Carter and Fowler, 'Phil. Mag.,' vol. 3, p. 27 (1927); see also Foote, Meggers and Mohler, 'Astrophys. J.,' vol. 55, p. 145 (1922), and Datta, 'Roy. Soc. Proc.,' A, vol. 101, p. 544 (1922).

As regards the occurrence of forbidden emission lines, it should be remarked that the average life-time of an atom emitting "quadripole radiation" is much longer than in the case of an ordinary dipole emission, and that, at any rate in the laboratory, it is quite possible that the atom would not remain undisturbed long enough for quadripole radiation to become effective.[†] In this case, quadripole radiation may not be an adequate explanation. Such a phenomenon would not, of course, arise in absorption.

2. A formula for the intensity of quadripole radiation appears to have been first given by Gaunt and McCrea,[‡] using an extension of Dirac's method of treating radiation by means of quantum mechanics. They apply their result to the case of a harmonic oscillator and a rigid rotator.

Using rather more classical ideas, an expression for the intensity of multipole radiation was derived by Rubinowicz,[§] who worked out the exact formula for the intensity of the Lyman series in hydrogen. More recently, Blaton[||] has applied the same method to the Balmer series. The main idea of the method is that a retarded vector potential is used, and that in the classical expression for the potential, the current density is taken to be the Schrödinger current density of wave mechanics associated with a given transition.

Let R be the distance from the point of observation to the scource of radiation of frequency ν, and let S be the current density. Then we define the vector potential, A, by[¶]

$$A = \frac{1}{c} e^{2\pi i\nu t} \int S \frac{e^{-ik\mathrm{R}}}{\mathrm{R}} \, d\tau,$$

the integral being taken throughout space; and the intensity of radiation in the z-direction, per unit solid angle, is given by[¶]

$$J = \frac{ck^2}{8\pi} |(\vec{z} \times A)|^2 = \frac{ck^2}{16\pi} (|A_x + iA_y|^2 + |A_x - iA_y|^2), \tag{1}$$

where $k = 2\pi\nu/c$, and $\vec{z}$ is a unit vector in the z-direction.

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[*] Bartlett, 'Phys. Rev.,' vol. 34, p. 1247 (1929).

[†] *Cf.* Bartlett, *loc. cit.*

[‡] Gaunt and McCrea, 'Proc. Camb. Phil. Soc.,' vol. 23, p. 930 (1927).

[§] Rubinowicz, 'Phys. Z.,' vol. 29, p. 817 (1928); 'Z. Physik,' vol. 53, p. 267 (1929).

[||] Blaton, 'Z. Physik,' vol. 61, p. 263 (1930).

[¶] Rubinowicz, 'Phys. Z.,' *loc. cit.*

Denoting by r the distance of the point of observation from the centre of the atom, taken as origin, we may write $R = r - z$, and, omitting the time factor,†

$$A = \frac{e^{-ikr}}{r}\int S\, e^{ikz}\, d\tau = \frac{e^{-ikr}}{cr}\left[\int S\, d\tau + ik\int zS\, d\tau + \ldots\right]. \tag{2}$$

The first integral in the last expression gives the dipole contribution to the intensity, the second the quadripole contribution, etc. From (1) and (2) we have for the intensity of quadripole radiation

$$J = \frac{\pi^3\nu^4}{c^5}\left[\left|\int z\,(S_x + iS_y)\, d\tau\right|^2 + \left|\int z\,(S_x - iS_y)\, d\tau\right|^2\right]. \tag{3}$$

3. Let us now assume that we are dealing with a one-electron problem in a central field of force, and consider a transition from a state denoted by ψ_1 to one denoted by ψ_2 (we shall always use a suffix 1 to denote the initial, and 2 the final state). Then the associated Schrödinger current density is

$$S = \frac{he}{4\pi i m_0}(\psi_1 \operatorname{grad} \psi_2^* - \psi_2^* \operatorname{grad} \psi_1), \tag{4}$$

where ψ^* is the conjugate of ψ.

From (3) and (4), and noting that

$$\int z\psi_1 \frac{\partial \psi_2^*}{\partial x}\, d\tau = -\int z\psi_2^* \frac{\partial \psi_1}{\partial x}\, d\tau,$$

etc., we have for J,

$$J = \frac{\pi h^2 e^2 \nu^4}{4 m_0^2 c^5}(X_1 + X_2), \tag{5}$$

where

$$X_1 = \left|\int z\psi_1 \left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right)\psi_2^*\, d\tau\right|^2$$

$$X_2 = \left|\int z\psi_1 \left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right)\psi_2^*\, d\tau\right|^2,$$

the integrals being taken throughout space.

Taking polar co-ordinates, let l, m denote respectively the azimuthal and magnetic quantum numbers for the state ψ_1, and l', m' the corresponding numbers for the state ψ_2. Then we may write, with the usual notation

$$\psi_1 = R_1 P_l^m (\cos\theta)\, e^{-im\phi},$$

$$\psi_2^* = R_2 P_l^m (\cos\theta)\, e^{+im\phi},$$

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† *Cf.* Bartlett, *loc. cit.*

where R_1, R_2 depend on r only. We shall require the following formulæ for spherical harmonics:

$$\left.\begin{aligned}
&\left(\frac{\partial}{\partial x}+i\frac{\partial}{\partial y}\right)\psi_2^* \\
&\qquad=\frac{e^{i(m'+1)\phi}}{2l'+1}\left[\left(\frac{dR_2}{dr}-\frac{l'}{r}R_2\right)P_{l'+1}^{m'+1}-\left(\frac{dR_2}{dr}+\frac{l'+1}{r}R_2\right)P_{l'-1}^{m'+1}\right] \\
&\left(\frac{\partial}{\partial x}-i\frac{\partial}{\partial y}\right)\psi_2^* \\
&\qquad=\frac{e^{i(m'-1)\phi}}{2l'+1}\left[-(l'-m'+1)(l'-m'+2)\left(\frac{dR_2}{dr}-\frac{l'}{r}R_2\right)P_{l'+1}^{m'-1}\right. \\
&\qquad\qquad\left.+(l'+m')(l'+m'-1)\left(\frac{dR_2}{dr}+\frac{l'+1}{r}R_2\right)P_{l'-1}^{m'-1}\right] \\
&\int_0^\pi P_l^m P_{l'}^m \sin\theta\cos\theta\,d\theta=0\quad(l'\neq l\pm 1) \\
&\qquad\qquad=\frac{2}{(2l+1)(2l+3)}\,\frac{(l+m+1)!}{(l-m)!} \\
&\qquad\qquad\qquad\qquad(l'=l+1) \\
&\int_0^\pi (P_l^m)^2\sin\theta\,d\theta=\frac{2}{2l+1}\,\frac{(l+m)!}{(l-m)!}
\end{aligned}\right\}. \tag{6}$$

The first two are equivalent to some given by Darwin[†] and may be proved from known properties of spherical harmonics; the last two are well known.

On substituting from (6) in (5), we find that X_1 and X_2 both vanish unless $l'=l$ or $l\pm 2$, and $m'=m\pm 1$. Thus the selection rules for quadripole radiation in the z-direction are

$$\Delta l=0,\ \pm 2;\quad \Delta m=\pm 1.$$

The z-direction has, of course, here been specialised. Taking account of the other two directions, the general selection rules are easily seen to be $\Delta l=0,\ \pm 2$, $\Delta m=0,\ \pm 1$, as compared with $\Delta l=\pm 1$, $\Delta m=0,\ \pm 1$, in the ordinary case. These results also follow immediately when the intensity is expressed as a matrix, as in Gaunt and McCrae's result.

4. We take first the case $\Delta l=+2$ (the case $\Delta l=-2$ is evidently deducible from this). Putting $l'=l+2$ and $m'=m-1$, say, we find without difficulty with the use of (6), and inserting the normalisation for the θ, ϕ part of the integration,

$$X_1=\frac{(l+m+1)(l-m+1)(l-m+2)(l-m+3)}{(2l+1)(2l+3)^2(2l+5)}I^2;\quad X_2=0, \tag{7}$$

[†] Darwin, 'Roy. Soc. Proc.,' A, vol. 118, p. 668 (1928).

where

$$I = \int_0^\infty \left[r^3 R_1 \frac{dR_2}{dr} + (l+3) r^2 R_1 R_2 \right] dr. \tag{8}$$

Similarly, taking $l' = l + 2$ and $m' = m + 1$, we find that $X_1 = 0$, while X_2 only differs from the above expression for X_1 in having the sign of m changed.

In the absence of a magnetic field, to find the total intensity (per atom) for a transition $\Delta l = +2$, we take the sum of the results for $\Delta m = \pm 1$, sum for m from $-l$ to $+l$, and average over all initial states, *i.e.*, divide by $2l+1$, the weight of the initial state. We thus find, from (5) and (7),

$$J = \frac{\pi h^2 e^2 \nu^4}{2m_0^2 c^5} \cdot \frac{(l+1)(l+2)}{5(2l+1)(2l+3)} \cdot I^2. \tag{9}$$

Consider now the case $\Delta l = 0$. Putting $l' = l$, $m' = m - 1$, say, in (5), and noting that in this case, on account of the orthogonality of the eigen functions, we have

$$\int_0^\infty r^2 R_1 R_2 \, dr = 0 \qquad (R_1 \neq R_2),$$

we find, using (6), and after normalising for θ and ϕ,

$$X_1 = \frac{(l+m)(l-m+1)(2m-1)^2}{(2l-1)^2(2l+3)^2} M^2 \; ; \quad X_2 = 0, \tag{10}$$

where

$$M = \int_0^\infty r^3 R_1 \frac{dR_2}{dr} dr = - \int_0^\infty r^3 R_2 \frac{dR_1}{dr} dr.$$

With $l' = l$, $m' = m + 1$, we find, as before, $X_1 = 0$, while X_2 only differs from the expression for X_1 in (10) in a change of sign of m. To find the total intensity for a transition $\Delta l = 0$, we must sum for m and average over all initial states, as before. Since $|m| \leqslant l$, the summation for m, in the case $m' = m - 1$, is now from $(-l+1)$ to l; on account of the factor $(l+m)$ in (10), however, this is the same as summing from $-l$ to $+l$, and similarly in the case $m' = m + 1$. We hence find for the intensity, from (10) and (5)

$$J = \frac{\pi h^2 e^2 \nu^4}{2m_0^2 c^5} \cdot \frac{2l(l+1)}{15(2l-1)(2l+3)} \cdot M^2. \tag{11}$$

An S → S transition ($l = 0$) is thus still "forbidden," even for quadripole radiation.*

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* *Cf.* Rubinowicz, *loc. cit.*

5. We shall now apply the results (9) and (11) to compare the intensities of the simplest types of "forbidden" transition, namely S → D and P → P, with that of the "allowed" transition S → P. Putting $l=0$ in (9) and (8), we have for the intensity of an S → D line, of frequency ν_1, say,

$$J_1 = \frac{\pi h^2 e^2 \nu_1{}^4}{15 m_0{}^2 c^5} I_1{}^2, \tag{12}$$

where

$$I_1 = \int_0^\infty \left(r^3 R_1 \frac{dR_2}{dr} + 3r^2 R_1 R_2 \right) dr = -\int_0^\infty r^3 R_2 \frac{dR_1}{dr}\, dr.$$

Or, writing $R = P/r$, and introducing "atomic" units, *i.e.*, $h^2/4\pi^2 m_0 e^2$ as unit of length,

$$I_1{}^2 = \frac{\left[\int_0^\infty \left(r \frac{dP_1}{dr} - P_1 \right) P_2\, dr \right]^2}{\int_0^\infty P_1{}^2\, dr \,.\, \int_0^\infty P_2{}^2\, dr}. \tag{13}$$

where we have now inserted the normalisation factor for r.

Now the ordinary (dipole) intensity of radiation in the z-direction for an S → P line, of frequency ν_2 say, is given by*

$$J_2 = \frac{4\pi^3 e^2 \nu_2{}^4}{3c^3} \left[\int_0^\infty r^3 R_1 R_2\, dr \right]^2 .$$

Or, introducing P and atomic units as before, and normalising,

$$J_2 = \frac{4\pi^3 e^2 \nu_2{}^4}{3c^3} \left(\frac{h^2}{4\pi^2 m_0 e^2} \right)^2 I_2{}^2, \tag{14}$$

where

$$I_2{}^2 = \frac{\left(\int_0^\infty P_1 P_2\, dr \right)^2}{\int_0^\infty P_1{}^2\, dr \,.\, \int_0^\infty P_2{}^2\, dr}. \tag{15}$$

From (12) and (14), the ratio of the intensity of an S → D line to that of an S → P line is

$$\frac{J_1}{J_2} = \tfrac{1}{5} \left(\frac{2\pi c^2}{hc} \right)^2 . \left(\frac{\nu_1}{\nu_2} \right)^4 . \frac{I_1{}^2}{I_2{}^2}, \tag{16}$$

I_1, I_2 are given by (13) and (15). P_1, P_2 refer, respectively, to an S and D state in I_1, and to an S and P state in I_2.

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* Sommerfeld, "Wellenmechanischer Ergänzungsband," p. 96. To conform to the above scheme Sommerfeld's expression must be multiplied by a factor $\frac{1}{2}$, due to taking a time mean. This result may also be obtained from (1) and (2) above.

(16) assumes, of course, that the lines S → D and S → P are both *emission* lines. For the case when they are *absorption* lines, using the well-known relation between the Einstein coefficients, namely, $A_{rs} = 8\pi h\nu^3/c^3 . B_{rs}$, we find for the ratio of the absorption intensities, in place of (16)

$$\frac{J_1}{J_2} = \tfrac{1}{5}\left(\frac{2\pi e^2}{hc}\right)^2 . \frac{\nu_1}{\nu_2} . \frac{I_1^2}{I_2^2} . \tag{17}$$

Taking now the case of a P → P transition, of frequency ν_1, say, (11) gives

$$J_1^2 = \tfrac{4}{75} \frac{\pi h^2 e^2 \nu_1^4}{m_0^2 c^5} I_3^2,$$

where

$$I_3^2 = \frac{\left[\int_0^\infty r P_2 \frac{dP_1}{dr} \, dr\right]^2}{\int_0^\infty P_1^2 \, dr . \int_0^\infty P_2^2 \, dr} .$$

For the intensity of a P → S line (instead of S → P) of frequency ν_2, the expression (14) must be multiplied by $\frac{1}{3}$, since the weight of the initial state is now 3 instead of 1. Hence the ratio of the (emission) intensity of a P → P line to that of a P → S line is

$$\frac{J_1'}{J_2'} = \tfrac{6}{25}\left(\frac{2\pi e^2}{hc}\right)^2 . \left(\frac{\nu_1}{\nu_2}\right)^4 \frac{I_3^2}{I_2^2}, \tag{18}$$

I_2 being given by (15).

6. Using (17), the numerical values of the absorption intensity ratio of 1S — 3D to that of 1S — 2P have been calculated for the first four of the alkalis, Hartree's method of self-consistent fields* being used to obtain tabulated values of the radial wave-functions P, the integrals I_1 and I_2 being then calculated by numerical integration; the experimental values of ν were used. The radial wave-functions for Rb have been calculated by Hartree, those for Na by McDougall, and those for the S and P terms for Li by Hargreaves,† the solution for hydrogen being used for the D term for Li as a sufficient approximation.

The necessary functions for K were calculated by the author from the self-consistent field obtained by Hartree. The calculation involves incidentally the determination of the eigen values ε ($\varepsilon = 1/n^2$ where n is the effective quantum number). The approximate calculated and observed values are given in Table I, the mean of the two term-values being taken for doublets. The agreement would be improved by adding in the spin and relativity corrections, though even then, as pointed out by Hartree, a smaller value than the observed is only to be expected on account of the fact that the polarisation of the atom-core by the series electron has been neglected.

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* Hartree, 'Proc. Camb. Phil. Soc.,' vol. 24, pp. 89, 111 (1928).

† Hargreaves, 'Proc. Camb. Phil. Soc.,' vol. 25, p. 15 (1929).

Table I.—Approximate Calculated and Observed Eigen values (ε) for Potassium.

Term.	1S.	2P.	3D.
Calculated	0·261	0·171	0·114
Observed	0·319	0·200	0·123

The values of I_1^2 and I_2^2 as found by numerical integration for the alkalis considered, together with the intensity ratio calculated from (17) and the experimental values for K and Rb, are given in Table II. The result for hydrogen, as calculated from Rubinowicz' formula (*loc. cit.*) is also given for comparison.

Table II.—Ratio of Absorption Intensities of (1S — 3D) to (1S — 2P).

Element.	Li.	Na.	K.	Rb.	H.
I_1^2	2·335	2·627	3·312	3·338	—
I_2^2	18·60	23·89	38·19	25·25	—
J_1/J_2 calculated	$2 \cdot 8 \times 10^{-6}$	$2 \cdot 0 \times 10^{-6}$	$1 \cdot 5 \times 10^{-6}$	$2 \cdot 1 \times 10^{-6}$	$1 \cdot 1 \times 10^{-6}$
J_1/J_2 observed	—	—	77×10^{-6} $1 \cdot 1 \times 10^{-6}$	85×10^{-6}	—

It will be seen that the calculated intensity ratios all lie close together. As regards the experimental values, the first value for K and that for Rb are taken from Sowerby and Barratt's paper (*loc. cit.*), while the second value for K is a result for the relative number of dispersion electrons given by Rasetti,* since the number of dispersion electrons per atom associated with a given frequency is proportional to the corresponding absorption intensity. Values for Li and Na do not, unfortunately, appear to be available, though, as stated before, the absorption line 1S — 3D has been observed for all the alkalis.

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* Rasetti, 'Atti Accad. Lincei,' vol. 6, p. 54 (1927).

While the agreement is far from good, it may perhaps be regarded as fairly satisfactory, considering the difficulty of estimating the relative intensities and the fact that the experimental values for K differ widely. Rasetti estimates the probable error of his result as 50 per cent.

The relative emission intensity of 3P → 2P to that of 3P → 1S has been calculated from (18) for the case of Rb only. The values found were :—

$$I_3{}^2 = 1\cdot288, \quad I_2{}^2 = 0\cdot4949, \quad J_1'/J_2' = 1\cdot6 \times 10^{-6}.$$

The corresponding ratio for hydrogen as calculated from Blaton's results (*loc. cit.*) is $6\cdot7 \times 10^{-8}$.

The series P → P does not appear to have been observed experimentally in the alkalis ; a few lines of this series are given in Fowler's " Report on Series in Line Spectra " for lithium, but these were doubtless due to external electric fields. In any case, since this series only occurs in emission, it seems probable, for the reason mentioned earlier, that this numerical result has not the same experimental value as those given for absorption.

I wish to express my thanks to Mr. R. H. Fowler for suggesting this problem, and for his helpful criticism ; I am also indebted to Dr. Hartree and Messrs. McDougall and Hargreaves for supplying me with the radial wave-functions mentioned above.

The Spectrum of Ionised Fluorine (F II).

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Introductory.

The first considerable list of lines due to singly-ionised fluorine (72 in number, extending from λ 4934 to λ 3145) was given in 1912 by Porlezza,* who obtained the spectrum by passing discharges through vacuum tubes containing silicon tetrafluoride. At that time it was not possible to assign the lines to the ionised atom, and Porlezza made no attempt to analyse the spectrum. About the same time, Exner and Haschek† recorded a list of lines, obtained from a spark between electrodes of carbon impregnated with potassium fluoride, which they attributed to fluorine. The list included a few of Porlezza's lines and a considerable number of others whose identity remains obscure. Excluding a few minor investigations, recorded in Kayser's "Handbuch der Spectroscopie," vol. 7, pp. 401–404, the next contribution of note towards our knowledge of this spectrum was made by Gale and Monk,‡ who obtained 24 of the lines given by Porlezza, as well as 6 others, from a spark discharge in fluorine gas. Although Gale and Monk did not attribute these lines to the ionised atom, they distinguished them from lines produced in vacuum tube discharges in fluorine which have since been shown to belong to the neutral atom. The first record of a spectrum definitely assigned to F^+ was made by de Bruin,§ about half of whose list of 71 lines between λ 4447 and λ 3057 were included in Porlezza's list. De Bruin discussed the possibility of analysis of the spectrum, but his data, as it now appears, were insufficient to permit of any satisfactory results.

Up to now, therefore, the spectrum has been very imperfectly known, and the present investigation (which forms part of a general research on the successive spectra of fluorine, of which some of the results have already been published‖) was undertaken in the hope of obtaining more definite knowledge.

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* 'Gaz. Chim. Ital.,' vol. 42, Part 2, p. 42 (1912).

† "Die Spektren der Elemente bei normalen Druck," 2nd ed., vol. 3 (1912).

‡ 'Astrophys. J.,' vol. 59, p. 125 (1924).

§ 'Arch. Néerl. Sci. Exp. Nat.,' vol. 3, A, p. 70 (1928).

‖ F I, 'Roy. Soc. Proc.,' A, vol. 113, p. 323 (1926), and vol. 117, p. 407 (1928); F III, *ibid.*, vol. 122, p. 144 (1929).

469 lines have been obtained, of which nearly 200 have been classified. The most prominent lines are those given by Porlezza, Gale and Monk, and de Bruin, and de Bruin's assignment of the spectrum to the singly ionised atom has been confirmed. The large addition to the lists of those authors is due partly to the inclusion of fainter lines and the extension of the spectrum beyond the limits of their work, but also in a considerable degree to the use of high resolving power, by which several lines previously recorded as single have been found to be multiple. For example, λ 4103 has been resolved into five components, λλ 4447, 4207 into three each, and the "triplets" at λ 3500 and λ 3900 into nine and five, respectively. It should be mentioned also that some of Porlezza's and de Bruin's lines have not been confirmed. While some of the fainter lines now recorded might well be due to undetected impurities, there is no doubt that the great majority belong to F II.

Experimental Arrangements.

The spectrum was obtained by passing powerful discharges through silicon tetrafluoride in vacuum tubes; details of the methods employed are given in the first paper on the F I spectrum (*loc. cit.*). The lines of F II cannot be produced at greatest intensity with reasonable exposures without a considerable development of F III, and it has not been possible, therefore, always to distinguish with confidence between the two spectra so far as the faintest lines are concerned. Some of the lines now given have already been recorded as belonging to F III, but further investigation has shown that they are due to the singly-ionised atom. Such lines have been indicated in Table I by a footnote. The possibility that some of them belonged to F II was stated in the paper on F III.

The instruments employed were:—(1) The Willis glass spectrograph (for the region λ 8400–λ 3900), giving a dispersion varying from 60 A. per millimetre at λ 8000 to 4·5 A. per millimetre at λ 3900; (2) the Hilger quartz Littrow spectrograph (for the region λ 4000 to λ 2200), giving a dispersion varying from 11·5 A. per millimetre at λ 4000 to 2 A. per millimetre at λ 2300; (3) the 10-foot concave grating mounted at first in the Abney, and later in the Eagle, manner (for all of the above-mentioned regions for which high resolution was necessary). This instrument was used in the first five orders, according to requirements; (4) the vacuum concave grating spectrograph (for the region λ 2200 to λ 1200), giving an approximately normal dispersion of 17·5 A. per millimetre. Eastman neo-cyanin plates were used for the infra-red and Schumann plates for the extreme ultra-violet. Exposures ranging up to 13 hours were given.

Most of the lines were measured with reference to the iron arc spectrum, using the standards recommended by the International Astronomical Union in 1922 when possible and the measures of Burns when additional standards were required. The faint lines, however, were measured by interpolation with reference to the previously measured stronger ones supplemented by lines of silicon and whatever well-measured impurity lines happened to appear. This was necessary, as the superposition of a comparison spectrum tended to obscure such lines. In the Schumann region, several lines of carbon, silicon and aluminium, which had been measured by Bowen or Smith and Lang, appeared in the spectra and were used as standards. Except in this region and the infra-red, the wave-lengths given for all but the faintest lines are weighted means of values obtained from several plates, and should not be much in error. The most accurate wave-lengths are given in the table to three places of decimals.

Silicon and impurity lines were detected as far as possible by reference to all available tables, and also by a comparison of their behaviour on different plates. As the result of the latter procedure several lines were eliminated for which no assigned origin could be found, and it is therefore probable that some of the faintest tabulated lines, which appeared only on the strongest plate, should also be removed from the list. In the absence of any method of identifying them, however, all such lines have been included in case they should subsequently turn out to be significant.

Table I contains the lines which, with the above-mentioned reservation, can be assigned with considerable confidence to F II. The eight lines in the infra-red are subject to an additional uncertainty since the silicon spectrum has not been thoroughly explored in this region. The lines in question, if due to silicon, arise from the doubly or still more highly ionised atom, and it remains uncertain whether they are to be so attributed or are genuine F II lines. In the Schumann region several hundred lines have been obtained whose origins cannot yet be assigned with certainty. There is a far greater chance of impurities escaping detection in this region, and the conditions of production of the lines in sufficient intensity allow of the possibility of F III, F IV and Si V being well represented. Only those Schumann lines, therefore, have been given in Table I which analysis shows to be certainly due to F II. For the sake of completeness, nine lines and an unresolved group recorded by Bowen* in the extreme ultra-violet have been included also.

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* ' Phys. Rev.,' vol. 29, p. 231 (1927).

The intensities given in the table are eye estimates of the blackening of the photographic plate. No correction has been made for varying sensitivity of different brands of plate or of any brand for different wave-lengths, and, owing to the wide gaps separating the lines in the Schumann, the visible and near ultra-violet, and the infra-red regions, it has not been possible to correlate even the darkening of the plates in one of these regions with that in another. Within each region, however, the figures are roughly accurate.

Table I.—Lines of Singly-Ionised Fluorine (F II).

λ (Int.).	ν.	Combinations.
* 8346·7 (00)	11977·5	
8231·0 (3*n*)	12145·8	
14·6 (½)	170·0	
8150·4 (0)	266·0	
8058·1 (00)	406·4	
22·4 (1*n*)	461·6	
16·6 (3*n*)	470·7	
7917·8 (0)	626·2	
6763: (4*n*)†	14782:	
5589·31 (0)	17886·3	$3p\,^1D_2{}^b - 3d\,^1P_1{}^b$
5173·16 (2)	19325·2	$3p\,^1D_2{}^b - 3d\,^1D_2{}^b$
10·85 (1)‡	560·8	
5001·98 (3)	986·5	$3p\,^1D_2{}^a - 3d\,^1D_2{}^a$
4933·25 (5)	20265·0	$3p\,^1D_2{}^a - 3d\,^1P_1{}^a$
4859·37 (7)	573·1	$3s\,^1D_2{}^a - 3p\,^1F_3{}^a$
4738·0 (0)	21100·2	
34·37 (2)	116·2	$3p\,^1D_2{}^a - 3d\,^1F_3{}^a$
30·6 (00)	133·2	
07·9 (0*n*)	235·0	
01·3 (0)§	264·8	
4638·2 (0)	554·0	
02·1 (00)	723·1	
4576·1 (0)	846·5	
53·95 (½)	952·8	
29·2 (½*n*)	22072·6	
27·3 (2*n*)	081·9	
22·1 (1½*n*)	107·3	
20·3 (0*n*)	116·1	
18·4 (½*n*)	125·4	
12·6 (0*n*)	153·8	
10·2 (½*n*)	165·6	
07·0 (1*n*)	181·3	
05·9 (1½*n*)‖	186·7	
00·9 (1*n*)	211·4	

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* Possibly due to silicon.

† This line has previously been recorded in the list of F I lines (*loc. cit.*) where a note was made of its peculiar behaviour. It seems probable that there is a broad F II line superposed on a close pair of F I lines.

‡ ? impurity.

§ ? O II.

‖ ? Double.

Table I—(continued).

λ (Int.).	ν.	Combinations.
4497·0 (0)	22230·6	
95·9 (0)	236·1	
88·2 (½r)	274·2	
86·5 (½n)	282·6	
85·2 (½n)	289·1	
83·6 (½n)	297·0	
79·9 (1n)	315·5	
78·2 (½n)	323·9	
75·2 (½n)	338·9	
71·1 (½n)	359·4	
69·9 (1n)	365·4	
69·5 (1n)	367·4	$3p\ {}^3P_2 - 3s\ {}^3P_2{}^b$
67·9 (0n)	375·9	
66·2 (½n)	384·4	
65·5 (½n)	387·9	
64·0 (1n)	395·4	
62·0 (0n)	405·5	
47·18 (12n)	479·9	$3d\ {}^3D_3 - 4f\ {}^3F_{432}$
46·71 (10n)	482·3	$D_2 - \quad F_{432}$
46·51 (6n)	483·3	$D_1 - \quad F_{432}$
34·9 (1n)	542·3	
33·8 (0)	547·9	
32·3 (1n)	555·5	
27·2 (1n)	581·5	
23·7 (½n)	599·4	
22·7 (½n)	604·5	
21·5 (½n)	610·6	
20·9 (½n)	613·7	
20·2 (1n)	617·3	
14·2 (0n)	648·0	
10·6 (½n)	666·5	
05·5 (1n)	692·7	
04·0 (1n)	700·4	
00·57 (1)*	718·0	
4398·3 (½n)	729·9	
97·6 (0n)	733·5	
88·6 (0n)	780·1	
86·8 (1n)	789·4	
68·9 (0)	882·8	
68·34 (1)†	885·6	
43·6 (0)‡	23016·0	
41·9 (0n)§	025·0	
38·50 (½)*	043·0	
32·7 (00)	073·9	
28·2 (1r)	097·9	
27·5 (0)§	101·6	
22·0 (½n)	131·0	
21·0 (0n)	136·4	
18·9 (½n)	147·6	
17·3 (3n)	156·2	$3p\ {}^3D_3{}^b - 3d\ {}^3D_{32}$
15·3 (½n)	166·9	
14·2 (½n)	172·8	$D_2{}^b - \quad D_{32}$
12·8 (½n)	180·3	$D_1{}^b - \quad D_{21}$
12·1 (½n)	184·1	
10·2 (½n)	194·3	
09·1 (0n)	200·4	

* ? Impurity.
† ? Oxygen.
‡ ? Chlorine.
§ ? O II.

Table I—(continued).

λ (Int.).	ν.	Combinations.
4299·177 (10)	23253·75	$3s\,^1D_2^a - 3p\,^1P_1^a$
87·5 (0*n*)	317·1	
85·3 (1*n*)	329·1	
82·9 (0*n*)	342·1	
82·0 (1*n*)	347·0	
81·3 (0*n*)	350·9	
78·89 (4*n*)	364·0	$3p\,^3D_1^b - 3d\,^3F_{432}^b$
77·51 (6*n*)	371·5	$D_2^b - F_{432}^b$
75·21 (8*n*)	384·1	$D_3^b - F_{432}^b$
71·1 (1*n*)	406·6	
50·3 (1*n*)	521·1	
48·4 (0*n*)	531·6	
46·16 (15*n*)	544·1	$3d\,^5D_{4-0} - 4f\,^5F_{5-1}$
44·1 (1*n*)	555·5	
39·2 (0*n*)	582·7	
25·12 (4*n*)	661·3	
24·57 (0)	664·4	
23·7 (1*n*)	669·2	
23·4 (½*n*)	670·9	
23·0 (0*n*)	673·1	
22·2 (½*n*)	677·6	
18·6 (1*n*)	697·8	
17·9 (1½*n*)	701·7	
17·0 (0*n*)	706·8	
16·3 (0*n*)	710·7	
07·87 (2)	758·3	$3s\,^3P_0^b - 3p\,^3S_1^b$
07·442 (5)	760·74	$P_1^b - S_1^b$
07·162 (7)	762·32	$P_2^b - S_1^b$
4192·62 (2)	844·7	X $- 3p\,^1S_0^b$
86·1 (0)	881·7	
83·0 (00)	899·4	
26·96 (2)	24224·1	$3p\,^1D_2^a - 4s\,^1D_2^a$
19·219 (7)	269·63	$3s\,^3D_1^a - 3p\,^3D_1^a$
18·756 (3)	272·35	$D_1^a - D_2^a$
17·008 (5)	282·66	$D_2^a - D_1^a$
16·547 (7)	285·38	$D_2^a - D_2^a$
12·975 (5)	306·46	$D_3^a - D_2^a$
12·734 (4)	307·89	$D_2^a - D_3^a$
09·173 (8)	328·95	$D_3^a - D_3^a$
03·871 (7)	360·39	$3p\,^3P_2 - 3d\,^3D_2$
03·724 (7)	361·26	$P_0 - D_1$
03·525 (15)	362·45	$P_2 - D_3$
03·217 (5)	364·27	$P_1 - D_1$
03·085 (10)	365·05	$P_1 - D_2$
4093·3 (½)	423·0	
83·919 (6)	479·39	
59·3 (0)	628·1	
27·1 (½)	825·0	
26·6 (½)	828·1	
25·495 (15)	834·68	$3s\,^3S_1 - 3p\,^3P_0$
25·010 (10)	837·67	$S_1 - P_1$
24·727 (20)	839·41	$S_1 - P_2$
3974·791 (6)	25151·47	$3s\,^3P_2^b - 3p\,^3D_3^b$
72·670 (4)	164·89	$P_1^b - D_2^b$
72·411 (1)	166·53	$P_2^b - D_2^b$
72·047 (3)	168·84	$P_0^b - D_1^b$
71·626 (2)	171·51	$P_1^b - D_1^b$
63·6 (0)	222·6	
56·0 (1*n*)	271·0	
52·26 (2)	294·9	$3p\,^1P_1^b - 3d\,^1P_1^b$

Table I—(continued).

λ (Int.).	ν.	Combinations.
3945·65 (4)	25337·2	$3p\,{}^3P_0{}^a - 3d\,{}^3D_1{}^a$
44·33 (6)	345·7	$P_1{}^a - D_2{}^a$
41·52 (3)	363·8	$P_1{}^a - D_1{}^a$
39·03 (7)	379·8	$P_2{}^a - D_3{}^a$
35·00 (3)	405·8	$P_1{}^a - D_2{}^a$
33·0 (0)	418·8	
32·6 (0)	421·4	
30·6 (0)	434·3	
21·2 (0)	495·3	
20·6 (½)	499·2	
03·819 (4)	608·71	$3s\,{}^3D_1{}^a - 3p\,{}^3F_2{}^a$
01·955 (5)	620·95	$D_2{}^a - F_3{}^a$
01·852 (2)	621·62	$D_2{}^a - F_2{}^a$
00·8 (0)	628·5	$3p\,{}^3P_0{}^b - 3d\,{}^3P_1{}^b$
3898·833 (6)	641·46	$3s\,{}^3D_3{}^a - 3p\,{}^3F_4{}^a$
98·725 (2)	642·18	$D_3{}^a - F_3{}^a$
96·66 (3)	655·8	$3p\,{}^3P_2{}^b - 3d\,{}^3P_2{}^b$
96·12 (1)	659·3	$P_1{}^b - P_1{}^b$
93·04 (2)	679·6	$P_1{}^b - P_2{}^b$
76·1 (½*n*)	791·8	
51·667 (10)	955·45	$3s\,{}^5S_2 - 3p\,{}^5P_1$
49·987 (15)	966·78	$S_2 - P_2$
47·086 (20)	986·36	$S_2 - P_3$
41·26 (½)	26025·7	
38·25 (0)*	046·1	
37·59 (½)	050·6	
33·1 (1*n*)	081·1	
27·68 (½)	118·1	
23·8 (0)	144·5	
21·5 (2*n*)	160·2	
20·2 (0)†	169·1	
18·52 (2)	180·8	$3p\,{}^3P_0{}^a - 3d\,{}^3S_1{}^a$
14·65 (4)	207·3	$P_1{}^a - S_1{}^a$
05·90 (5)	267·5	$P_2{}^a - S_1{}^a$
01·09 (3)	300·8	$3p\,{}^3P_1{}^a - 3d\,{}^3P_2{}^a$
3798·46 (3)	319·0	$P_0{}^a - P_1{}^a$
94·60 (2)	345·8	$P_1{}^a - P_1{}^a$
92·40 (4)	361·1	$P_2{}^a - P_2{}^a$
92·12 (1)	363·0	$P_1{}^a - P_0{}^a$
85·97 (2)	405·9	$P_2{}^a - P_1{}^a$
81·63 (1)	436·1	
65·8 (0)‡	547·0	
56·5 (0)	612·7	
53·3 (0)	635·4	
52·36 (1)	642·4	
48·79 (½)	667·7	
39·60 (4)	733·2	$3p\,{}^1P_1{}^b - 3d\,{}^1D_2{}^b$
37·8 (0)	745·8	
20·30 (1)	872·0	
18·2 (0)‡	886·8	
13·96 (½)	917·8	
10·365 (4)	943·89	
06·63 (½)	971·1	
04·51 (8)	986·5	$3p\,{}^3F_{432}{}^a - 3d\,{}^3G_{543}{}^a$
3691·7 (00)	27079·9	
89·9 (0*n*)	093·5	
83·2 (0)	142·8	
82·01 (½)	151·4	

* ? Mg I. † ? Chlorine. ‡ ? Argon.

Table I—(continued).

λ (Int.).	ν.	Combinations.
3679·67 (5)	27168·7	$X - 3p\,{}^1P_1^b$
72·8 (00)	219·6	
70·17 (½)	239·0	
68·9 (0)	248·6	
68·12 (1)	254·2	
67·57 (½)	258·3	
61·8 (0)	301·0	
60·3 (0)	312·6	
56·91 (1*n*)	337·7	
56·50 (½)	340·8	
42·798 (7)	443·63	$3p\,{}^3F_{32}^a - 3d\,{}^3F_2^a$
41·985 (8)	449·75	F_{32}^a — F_3^a
41·011 (3)	457·10	F_3^a — F_4^a
40·891 (9)	458·00	F_4^a — F_4^a
33·2 (0)	516·3	
31·19 (½)	531·4	
29·86 (½)	541·5	
20·7 (00)	611·3	
12·33 (1)*	675·1	
08·89 (3)	701·5	$3s\,{}^3P_1^b - 3p\,{}^3P_0^b$
07·32 (3)	713·5	P_0^b — P_1^b
06·80 (4)	717·5	P_{21}^b — P_1^b
03·72 (6)	741·2	P_{21}^b — P_2^b
02·85 (8)†	747·9	
01·403 (7)	759·07	
3598·704 (7)	779·89	
95·917 (5)	801·42	
90·63 (7)†	842·4	
89·345 (6)	852·31	
87·980 (5)	862·91	
87·42 (3)	867·3	
87·13 (3)	869·5	
86·61 (1)*	873·6	
77·23 (2)	946·6	$3p\,{}^1P_1^a - 3d\,{}^1D_2^a$
74·92 (3)	964·7	$3p\,{}^3F_{432}^a - 3d\,{}^3D_3^a$
74·1 (0)	971·1	
71·68(3)	990·0	$3p\,{}^3F_{32}^a - 3d\,{}^3D_2^a$
69·47 (2)	28007·4	$3p\,{}^3F_2^a - 3d\,{}^3D_1^a$
63·87 (0)	051·4	
48·5 (½)	173·0	$3p\,{}^3D_1^b - 3d\,{}^3P_0^b$
46·6 (0)	188·3	$3p\,{}^3D_1^b - 3d\,{}^3P_1^b$
46·06 (1)	192·3	$3s\,{}^3D_1^a - 3p\,{}^3P_2^a$
45·5 (½+)	196·6	$3p\,{}^3D_2^b - 3p\,{}^3P_1^b$
44·392 (3)	205·55	$3s\,{}^3D_2^a - 3d\,{}^3P_2^a$
41·937 (8)	225·11	$3p\,{}^1P_1^a - 3d\,{}^1P_1^a$
41·765 (9)	226·48	$3s\,{}^3D_3^a - 3p\,{}^3P_2^a$
39·45 (1)	244·9	$3p\,{}^3D_3^b - 3d\,{}^3P_2^b$
38·474 (3)	252·72	$3s\,{}^3D_1^a - 3p\,{}^3P_1^a$
36·838 (7)	265·79	$3s\,{}^3D_2^a - 3p\,{}^3P_1^a$
35·162 (4)	279·19	$3s\,{}^3D_1^a - 3p\,{}^3P_0^a$
32·99 (½)‡	296·6	
32·2 (0)	302·9	
31·7 (0)	307·0	
30·6 (0)	315·8	
24·6 (00)	364·0	
22·883 (6)	377·75	$3s\,{}^1P_1^b - 3p\,{}^1S_0^b$
16·32 (2*r*)	430·7	
12·8 (0)	459·2	

* ? Impurity. † ? Double. ‡ ? Sodium.

Table I—(continued).

λ (Int.).	ν.	Combinations.
3505·763 (4)	28516·33	
05·614 (15)	517·55	$3p\ ^5P_3 - 3d\ ^5D_4$
05·508 (6)	518·41	$P_3 -$ D_3
03·095 (12)	538·06	$P_2 -$ D_3
02·954 (8)	539·20	$P_2 -$ D_2
02·859 (4)	539·97	$P_2 -$ D_1
01·562 (5)	550·54	$P_1 -$ D_2
01·487 (3)	551·15	$P_1 -$ D_1
01·416 (10)	551·74	$P_1 -$ D_0
3493·215 (2)	618·76	$3p\ ^1S_0{}^b - 3d\ ^1P_1{}^b$
76·2 (0)	758·8	$3p\ ^3D_3{}^a - 3d\ ^3F_2{}^a$
75·68 (2)	763·2	$D_3{}^a -$ $F_3{}^a$
74·800 (7)	770·43	$D_3{}^a -$ $F_4{}^a$
73·621 (2)	780·19	$D_2{}^a -$ $F_2{}^a$
73·314 (5)	782·74	$D_1{}^a -$ $F_2{}^a$
72·964 (6)	785·63	$D_2{}^a -$ $F_3{}^a$
70·2 (0*n*)	808·5	
68·23 (1)	824·9	
59·8 (0)	895·1	
58·4 (0*n*)	906·8	
53·8 (0)	945·2	$3p\ ^3F_3{}^a - 3d\ ^3P_2{}^a$
52·5 (½*n*)	956·1	
49·1 (0)	984·7	
46·64 (½)	29005·5	
45·68 (½)	013·6	
43·36 (1*n*)†	033·1	
42·5 (0)	040·2	
41·8 (0)	046·1	
39·9 (0)	062·2	
39·2 (0)	068·1	
36·57 (4)	090·5	
33·69 (1)	114·9	
26·34 (2)	177·3	
17·21 (4)*	255·3	
17·02 (6)	256·9	$3p\ ^3P_2 - 4s\ ^3S_1$
16·80 (1)	258·8	$P_0 -$ S_1
16·58 (4)	260·6	
16·45 (4)	261·8	$P_1 -$ S_1
14·663 (5)	277·09	$3p\ ^3D_3{}^a - 3d\ ^3D_3{}^a$
12·04 (2)	299·6	$D_2{}^a -$ $D_3{}^a$
11·66 (3)	302·8	$D_3{}^a -$ $D_2{}^a$
10·82 (1½)	310·0	
09·02 (3)	325·5	$D_2{}^a -$ $D_2{}^a$
08·68 (1½)	328·5	$D_1{}^a -$ $D_2{}^a$
06·83 (1)	344·5	$D_2{}^a -$ $D_1{}^a$
06·56 (2)	346·8	$D_1{}^a -$ $D_1{}^a$
05·980 (4)	351·74	
01·62 (2)	389·4	
3399·29 (3*n*)	409·5	$3p\ ^3P_2{}^b - 3d\ ^3D_3{}^b$
98·78 (1*n*)	413·9	$P_2{}^b -$ $D_2{}^b$
96·63 (1*n*)	432·5	
95·77 (1*n*)†	440·0	$P_1{}^b -$ $D_{21}{}^b$
94·22 (2*n*)†	453·4	$P_0{}^b -$ $D_1{}^b$
93·40 (1)‡	460·5	
91·8 (0)§	474·2	
79·29 (2)	583·5	$3p\ ^3S_1{}^b - 3d\ ^3P_0{}^b$
77·44 (4)	599·7	$S_1{}^b -$ $P_1{}^b$
73·49 (5)	634·4	$S_1{}^b -$ $P_2{}^b$

* Doubtful line. † ? Double. ‡ ? Impurity. § ? Argon.

Table I—(continued).

λ (Int.).	ν.	Combinations.
3372·24 (1)	29645·3	
71·65 (0)	650·5	
67·65 (1)	685·8	
64·48 (1)	713·8	
62·8 (0)	728·5	
61·2 (0)	742·6	
58·32 (4)	768·3	
57·82 (1)	772·7	
55·98 (3)	789·0	
54·34 (2)	803·6	
48·43 (½)	856·2	
47·74 (1)	862·3	
46·41 (½)	874·2	
24·13 (½)	30074·5	
23·57 (0)	079·5	
22·31 (1)	090·9	
21·30 (2)	100·1	
11·63 (1)	187·9	$3p\,{}^3\mathrm{D}_2{}^a - 3d\,{}^3\mathrm{S}_1{}^a$
08·91 (0)	212·8	
03·89 (6)	258·7	$3p\,{}^3\mathrm{D}_3{}^a - 3d\,{}^3\mathrm{P}_2{}^a$
01·41 (3)	281·4	$\mathrm{D}_2{}^a - \mathrm{P}_2{}^a$
00·09 (2*n*)†	293·5	
3296·56 (5)	325·9	$\mathrm{D}_2{}^a - \mathrm{P}_1{}^a$
96·19 (2)	329·3	$\mathrm{D}_1{}^a - \mathrm{P}_1{}^a$
94·37 (4)	346·1	$\mathrm{D}_1{}^a - \mathrm{P}_0{}^a$
86·25 (0)	421·1	
76·69 (0)	509·9	
70·49 (1)‡	567·7	
69·50 (½)	576·9	
64·16 (7)¶	626·9	$3p\,{}^1\mathrm{F}_3{}^a - 3d\,{}^1\mathrm{D}_2{}^a$
61·87 (0)	648·4	
54·82 (½)¶‡	714·8	
53·79 (0)¶	724·5	
53·42 (½+)¶	728·0	
53·11 (0)	730·9	
51·82 (0)§	743·2	
49·84 (0)§	761·9	
48·95 (0)	770·4	
47·58 (0)‖	783·3	
39·91 (½)	856·2	
38·10 (0)	873·4	
33·58 (1)‡	916·6	
30·89 (2*n*)	942·3	
29·47 (1*n*)	955·9	
29·00 (1½*n*)	960·4	
28·30 (1*n*)	967·1	
23·00 (½)	31018·0	
20·45 (0)	042·6	
19·33 (1)	053·4	
18·03 (½)	065·9	
15·10 (½)	094·2	
14·67 (½)	098·4	
09·34 (½)	150·1	
02·740 (10)	214·28	$3s\,{}^1\mathrm{D}_2{}^a - 3p\,{}^1\mathrm{D}_2{}^a$
01·17 (1)¶	229·6	
3194·67 (½)¶	293·1	
94·22 (½)¶	297·5	

† ? Double. ‡ ? Impurity. § ? Argon.
‖ ? Chlorine. ¶ Included in list of F III lines (*loc. cit.*).

Table I—(continued).

λ (Int.).	ν.	Combinations.
3192·26 (½)*	31316·8	
90·52 (0)	333·8	
72·81 (0)	508·8	
63·26 (0)*	603·9	
62·42 (1)†	612·3	
53·492 (6)	701·73	$3s\,{}^1\mathrm{P}_1^b - 3p\,{}^1\mathrm{P}_1^b$
47·965 (5)	757·38	$3p\,{}^1\mathrm{F}_3^a - 3d\,{}^1\mathrm{F}_3^a$
35·40 (0)	884·6	
30·3 (00)	936·6	
27·86 (0)	961·5	
25·73 (1*n*) } *	983·3	$3p\,{}^3\mathrm{D}_1^b - 3d\,{}^3\mathrm{D}_{21}^b$
25·59 (½*n*) }	984·7	$\mathrm{D}_2^b - \mathrm{D}_3^b$
25·15 (1*n*)*	989·2	$\mathrm{D}_2^b - \mathrm{D}_{21}^b$
24·19 (2*n*)*	999·1	$\mathrm{D}_3^b - \mathrm{D}_3^b$
20·12 (1*n*)*	32040·8	
18·69 (½*n*)*	055·5	
17·75 (0*n*)*	065·1	
06·16 (4*r*)	184·8	$3p\,{}^1\mathrm{P}_1^a - 4s\,{}^1\mathrm{D}_2^a$
3068·14 (0)†	583·6	
59·960 (8)	670·70	$3p\,{}^5\mathrm{P}_3 - 4s\,{}^5\mathrm{S}_2$
58·141 (7)	690·14	$\mathrm{P}_2 - \mathrm{S}_2$
57·083 (6)	701·44	$\mathrm{P}_1 - \mathrm{S}_2$
54·73 (0)‡	726·6	
48·80 (1)*	790·3	
46·26 (0)	817·7	
37·84 (0)§	908·6	
37·05 (0)	917·1	
23·98 (½)‡	33059·4	
15·16 (0)	156·1	
2992·30 (0)*	409·4	
88·45 (3*r*)*	452·4	
74·98 (00)	603·8	
73·78 (½*n*)	617·4	
70·3 (0*n*)	656·6	
67·4 (0)‖	689·5	
54·37 (½)	838·3	
47·27 (1*n*)	919·8	
36·48 (½)¶	34044·4	
04·61 (0)	418·0	
2894·30 (½)*	540·5	
92·93 (½)*	556·9	
91·13 (0)	578·4	$\mathrm{X} - 3p\,{}^1\mathrm{D}_2^b$
84·13 (1)‡	662·4	
78·72 (½)	727·5	
77·30 (½)	744·7	
76·49 (3)*	754·4	$3s\,{}^3\mathrm{D}_1^a - a\,{}^3\mathrm{P}_0^a$
75·88 (2)*	761·8	$\mathrm{D}_1^a - \mathrm{P}_1^a$
74·80 (4)*	774·9	$\mathrm{D}_2^a - \mathrm{P}_1^a$
74·22 (1)	781·9	$\mathrm{D}_1^a - \mathrm{P}_2^a$
73·13 (2)*	795·1	$\mathrm{D}_2^a - \mathrm{P}_2^a$
71·40 (5)*	816·0	$\mathrm{D}_3^a - \mathrm{P}_2^a$
67·30 (3)*	865·8	$3p\,{}^1\mathrm{F}_3^a - 4s\,{}^1\mathrm{D}_2^a$
57·20 (½*n*)	989·0	
56·74 (½)	994·7	
55·27 (½+)‡	35012·7	
42·89 (0)‡	165·2	
19·15 (0)	461·2	

* Included in list of F III lines (*loc. cit.*). † ? Impurity. ‡ ? Argon.
§ ? Chlorine. ‖ ? Mercury. ¶ ? Mg II.

Table I—(continued).

λ (Int.).	ν.	Combinations.
2803·97 (½)*	35653·3	
00·03 (0)*	703·4	
2798·79 (0)	719·3	
93·60 (0)	785·6	
87·38 (½)	865·4	
86·31 (½)	879·2	
84·00 (½*n*)	909·0	
83·58 (½*n*)	914·4	
83·25 (½*n*)	918·6	
62·11 (0)‡	36193·6	
59·86 (1)	223·1	
55·30 (1)	283·0	
52·80 (0)*	316·0	
51·74 (½)*	330·0	
2556·10 (4)	39110·3	$3s\,{}^1P_1{}^b - 3p\,{}^1D_2{}^b$
2329·93 (½)*	42906·6	$2p'\,{}^3P_2 - 3p\,{}^3P_2$
1747·40 (3)	57227·9	$3s\,{}^3S_1 - 3p\,{}^3P_2{}^a$
45·57 (2)	287·9	$S_1 - P_1{}^a$
44·86 (1)	311·2	$S_1 - P_0{}^a$
04·90 (½*n*)	58654·5	$3p\,{}^3P_2 - 3d\,{}^3S_1{}^a$
02·16 (0)	748·9	$3\rho\,{}^3P_2 - 3d\,{}^3P_2{}^a$
608·06 (8)**	164457	$2p\,{}^3P_1 - 2p'\,{}^3P_2$
607·48 (7)**	614	$P_0 - P_1$
606·95 (4)**	758	$P_1 - P_1$
606·81 (9)**	796	$P_2 - P_2$
606·27 (7)**	943	$P_1 - P_0$
605·67 (8)**	165106	$P_2 - P_1$
548·32 (2)**	182375	$2p\,{}^3P_0 - 3s\,{}^3S_1$
547·87 (3)**	525	$P_1 - S_1$
546·84 (4)**	869	$P_2 - S_1$
472 : ††	211860 :	$2p\,{}^3P_{210} - 3s\,{}^3D_{321}{}^a$

* Included in list of F III lines (*loc. cit.*).

** Measured and classified by Bowen.

‡ ? Argon.

†† Measured by Bowen.

Theoretical Structure of the Spectrum.

The electron structure of the F^+ ion in its ground state should be similar to that of the neutral oxygen atom, which is represented in the usual notation by $1s^2\,2s^2\,2p^4$. In an excited state, one of the $2p$ electrons would probably be raised to a higher energy level, and the spectrum would therefore be expected to be based on the ground configuration of the F^{++} ion, viz., an electron structure $1s^2\,2s^2\,2p^3$, corresponding to a stable ${}^4S$ state and metastable states, ${}^2P$, ${}^2D$. The terms of F II based on these three states will be referred to respectively as family A, family B and family C. By analogy with other light elements, however, the configuration $1s^2\,2s\,2p^5$ would also be expected to reveal itself by deep-lying terms, ${}^3P$ and ${}^1P$. The prominent terms to be looked for are therefore those in Table II, in the first and second columns of which n may have any value from 3 upwards when followed by s, p, or d, and from 4 upwards when followed by *f*. The most probable terms, of course, correspond to the smallest values of n.

Table II.—Theoretical Terms of the Spectrum F II.

Electron structure.	Terms.					
	Adopted prefix.	Term symbol.				
$1s^2\,2s^2\,2p^4$	$2p$	^3P	^1D		^1S	
$1s^2\,2s\;2p^5$	$2p'$		^3P	^1P		
		Core in ^4S state (Family A).	Core in ^2D state (Family B).		Core in ^2P state (Family C).	
$1s^2\,2s^2\,2p^3$ ns	ns	^5S ^3S	$^3D^a$	$^1D^a$	$^3P^b$	$^1P^b$
np	np	^5P ^3P	$^3F^a$ $^3D^a$ $^3P^a$	$^1F^a$ $^1D^a$ $^1P^a$	$^3D^b$ $^3P^b$ $^3S^b$	$^1D^b$ $^1P^b$ $^1S^b$
nd	nd	^5D ^3D	$^3G^a$ $^3F^a$ $^3D^a$ $^3P^a$ $^3S^a$	$^1G^a$ $^1F^a$ $^1D^a$ $^1P^a$ $^1S^a$	$^3F^b$ $^3D^b$ $^3P^b$	$^1F^b$ $^1D^b$ $^1P^b$
nf	nf	^5F ^3F	$^3H^a$ $^3G^a$ $^3F^a$ $^3D^a$ $^3P^a$	$^1H^a$ $^1G^a$ $^1F^a$ $^1D^a$ $^1P^a$	$^3G^b$ $^3F^b$ $^3D^b$	$^1G^b$ $^1F^b$ $^1D^b$
. .	.	.	.	.	.	.
. .	.	.	.	.	.	.
. .	.	.	.	.	.	.

Terms of the same type in family A, having successive values of n, form a Rydberg sequence and serve to determine numerical term values. In families B and C, however, term values so obtained must be decreased by approximately the difference between the $2p\,^4S$ and $2p\,^2D$, and the $2p\,^4S$ and $2p\,^2P$ terms of F III, respectively, in order to bring them to the same scale as those of family A. Conversely, if combinations between the three families of terms of F II can be detected, the differences between the term values on the same horizontal line in the three families, which are correlated by means of such combinations, will approximately indicate the magnitudes of the $2p\,^2D$ and $2p\,^2P$ terms of F III relative to the $2p\,^4S$ term.

Term Notation.

The notation of this paper is that used in the second paper on the F I spectrum (*loc. cit.*) and explained in detail by Prof. A. Fowler in his investigation of the O III spectrum,* except that, to save possible confusion with quantum numbers, the superscripts 1 and 2, denoting terms based on metastable states of the core, have been changed to *a* and *b*. Since such terms are frequently referred to, it has seemed better to use this notation than the more comprehensive system described by Russell, Shenstone and Turner,* in which the term-state of the core is included in brackets in the description of the term. Unfortunately the use of the superscript prohibits the inclusion of the symbol ° used to distinguish odd terms from even. It will be sufficient, however, to state that of the terms detected in the analysis, the $2p$, $3p$, $4f$ and aP terms are even, and the $2p'$, $3s$, $3d$, $4s$, and X terms are odd. In other respects the notation conforms to that recommended in the paper referred to.

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* ‘ Roy. Soc. Proc.,’ A, vol. 117, p. 317 (1928).

Analysis of the Spectrum.

The analysis of the spectrum has presented considerable difficulty owing to the smallness of the term separations and the unusual appearance of many of the multiplets. Although the lines were produced in vacuum tubes, where their sharpness is to some extent under control, very high dispersion had frequently to be employed, and even then the nature of the groups was not obvious owing to the non-appearance of the fainter members as a result of the low intensity. Further, the very strong silicon spectra which inevitably appeared tended to mask fainter fluorine lines, even at a distance of a few angstroms in the relatively low dispersion necessary to complete some of the wider groups. For example, at λ 4103 a multiplet of six lines is compressed within a range of less than an angstrom which contains strong lines of the unavoidable Si I and O II spectra as well as strong lines of nitrogen and argon, which were occasional impurities.

By a careful scrutiny of many plates, however, it has been possible to classify 173 lines. Of the remainder a large proportion is formed by a number of faint, nebulous lines between λ 4600 and λ 4200 which appear to be an associated group, probably arising from electron configurations not included in Table II. The character and close grouping of the lines makes the detection of multiplets among them difficult. Among the classified lines, whose combinations are set out in Tables III to VI, the multiplets $2p\,^3P - 2p'\,^3P$ and $2p\,^3P - 3s\,^3S$ were found by Bowen (*loc. cit.*). The remaining combinations, which are new, reveal, for each family of Table II, all the terms for which n = 3 (except $3d\,^1G^a$, $3d\,^1S^a$, and $3d\,^1F^b$, which could be guessed at but for which no corroborative evidence is possible) and also the terms $4s\,^5S$, $4s\,^3S$, $4s\,^1D^a$, $4f\,^5F$, $4f\,^3F$, as well as a few terms which appear to indicate other electron configurations. In addition, combinations between triplet terms of families

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* 'Phys. Rev.,' vol. 33, p. 900 (1929).

Table VI.—Combinations between Families A, B and C.

Combination.	λ (Int.).	ν.	Calculated value.
(*a*) Families A and B.			
$3s\,^3S_1 - 3p\,^3P_2{}^a$	1747·40 (3)	57227·9	57227·90
$^3S_1 - \quad ^3P_1{}^a$	45·57 (2)	287·9	288·14
$^3S_1 - \quad ^3P_0{}^a$	44·86 (1)	311·2	314·71
$3p\,^3P_2 - 3d\,^3S_1{}^a$	1704·90 ($\frac{1}{2}n$)	58654·5	58656·08
$3p\,^3P_2 - 3d\,^3P_2{}^a$	1702·16 (0)	58748·9	58749·66
$2p\,^3P_{210} - 3s\,^3D_{321}{}^a$	472 :	211860 :	211870
(*b*) Families A and C.			
$3p\,^3P_2 - 3s\,^3P_2{}^b$	4469·5 ($1n$)	22367·4	22367·22
$3d\,^3D_3 - 3p\,^3D_3{}^b$	4317·3 ($3n$)	23156·2	23156·24
$^3D_2 - \quad ^3D_3{}^b$			158·32
$^3D_3 - \quad ^3D_2{}^b$	14·2 ($\frac{1}{2}n$)	172·8	171·30
$^3D_2 - \quad ^3D_2{}^b$			173·38
$^3D_2 - \quad ^3D_1{}^b$	12·8 ($\frac{1}{2}n$)	180·3	179·98
$^3D_1 - \quad ^3D_1{}^b$			180·78

A and B, and, with less certainty, families A and C, have been found. All the triplet terms found can thus be given on the same scale of values. Combinations between the singlets of families B and C have not been recognised, nor have inter-combinations between any quintet, triplet and singlet terms. Four different scales of term values have therefore had to be employed (for the quintets, triplets, and two families of singlets, respectively), but, as will be explained, they are all probably of the right order of magnitude.

The numerical values of the terms are collected in Table VII, in comparison with those of O I. The principles on which they have been derived can best be explained in a description of the various families, which will now be given.

Family A.

This family, as would be expected, comprises the strongest lines in the spectrum, and the multiple terms, based as they are on a ^4S state of the F^{++} ion, have small separations. The triplet, $3s\,^3S - 3p\,^3P$, at λ 4025, is partially inverted and presents an unusual aspect for such a combination, being identical in appearance with an ordinary $^2P\,^2D$ group. The intervals and intensities in the $3p\,^5P - 3d\,^5D$ multiplet also are unusual, particularly in the weakness of the line $3p\,^5P_1 - 3d\,^5D_2$ and the excessive strength of $3p\,^5P_1 - 3d\,^5D_0$.

The abnormal weakness of the former line may be exaggerated by the intensity number assigned, as the group is very difficult to resolve, but unless there is a singlet superposed on the latter line it is certainly unexpectedly strong.

The family is analogous to the well-known quintet and triplet series systems of O I and, using series language, we may say that, including Bowen's $2p\,^3P - 3s\,^3S$ group, the first two members of the sharp and principal series of triplets and the sharp series of quintets have been found, as well as the first members of the principal, diffuse and fundamental series of quintets and the diffuse and fundamental series of triplets. Later members of these series would be expected in or near the Schumann region, where, from their small separations and the strong tendency of high level F II terms to diffuseness, they would appear as faint, nebulous single lines. Such lines can be found in likely positions, but since there is nothing to indicate when the right choice has been made, they have been left unguessed at.

Two sequences of terms containing two members each, viz., $2p\,^3P$, $3p\,^3P$ and $3s\,^3S$, $4s\,^3S$—are available for calculating the triplet terms. Assuming, as was done for F III, that the difference between the effective quantum numbers for the terms in each sequence is the same as that for other spectra derived from the same electron configuration and different nuclear charge (in this case, O I), we find from the P sequence that $2p\,^3P_2 = 275920$, and from the S sequence that $3s\,^3S_1 = 99640$, giving, from the observed line $2p\,^3P_2 - 3s\,^3S_1$, a value of $2p\,^3P_2 = 282329$. Giving the second value double weight since it is derived from higher level terms which follow a simple Rydberg formula almost exactly, we thus get a mean value of $2p\,^3P_2 = 280193$, which is probably very close to the true value. It corresponds to an ionisation potential of 34·6 volts. Turner,* from quite independent considerations, finds a probable ionisation potential of 34·5 volts for F^+, which is in excellent agreement with the value now found. All the other triplet term values of Table VII follow from observed lines.

The quintet terms have been evaluated in the same way from the sequence $3s\,^5S$, $4s\,^5S$, giving $3s\,^5S = 105536$. This sequence also is very nearly Rydbergian. The value is a very probable one, being, as for O I, slightly greater than that of the corresponding triplet term. Additional evidence that the term values are close to the truth is given by the magnitudes of the $4f\,^5F$ and $4f\,^3F$ terms (viz., 27487 and 25643), which are close to each other and to the quantity $4R/4^2 = 27434$.

Although not based on the ^4S state of the F^{++} ion, the terms $2p'\,^3P$ have been included in family A, since, so far as the evidence goes, they combine only with the terms of that family, and, in fact, only certainly with the $2p\,^3P$ term. The combination $2p'\,^3P - 3p\,^3P$, whose position can be calculated with an accuracy limited only by errors of measurement of lines, is doubtfully represented by a faint line (λ 2329·9) previously attributed to F III, falling three units from the calculated position of $2p'\,^3P_2 - 3p\,^3P_2$. The discrepancy is not prohibitive, since the $2p'\,^3P$ terms have been deduced from measurements in the extreme ultra-violet, but the identification has not been considered certain enough to justify an amendment of their values.

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* 'Phys. Rev.,' vol. 32, p. 727 (1928).

Family B.

This family, though not so conspicuous as the previous one, is well developed in F II. Most of the triplet terms are inverted, and one of the two normal ones ($3p\,^3D^a$) has the irregular separation ratio of 22·5 : 2·7. In addition to the predicted terms in Table II there is a triplet term, a $^3P_{210}$, of magnitude comparable with that of the $3p$ terms in this family, which appears to form a prominent combination with $3s\,^3D^a$. It does not, however, combine with the $3d$ terms, and it is possible, therefore, that the terms with which it combines are not $3s\,^3D^a$ but an unidentified set having the same separations. This, however, seems unlikely.

There is an element of uncertainty about the identification of the $3d\,^3G^a$ term since there is no check on it. It combines only with $3p\,^3F^a$, in which the separations are negligible, and the combination should therefore appear as a strong singlet. The line chosen is by far the most probable, the only alternative worth considering being an unclassified line at λ 3710 (ν 26944). This line, however, is much weaker than the one chosen, and is unlikely to be strong enough to represent a group of six lines.

The singlet terms are probably correctly identified, although, in the absence of multiple term separations, there is necessarily a greater chance of accidental numerical relations being mistaken for significant ones. All the lines involved are strong, however, and the intervals between them agree well within the limits of experimental error. The $3p$ terms have a much wider spread than the corresponding triplet terms, but the reverse is the case with the $3d$ terms. It should be noticed that the $3p\,^1F^a$ and $3p\,^1P^a$ terms can be interchanged if the $3d\,^1F^a$ and $3d\,^1P^a$ terms are interchanged at the same time.

The values of the triplet terms are given on the scale of the triplets of family A. This has been made possible by the detection of combinations between the two families in the Schumann region (see Table VI). When these combinations were found it became possible to classify a "rather weak, partially resolved group at λ 492" (ν 211860:) found by Bowen (*loc. cit.*) and suggested by him as possibly being the combination $2p\,^3\mathrm{P} - 3d\,^3\mathrm{D}$. It is now seen that it is actually $2p\,^3\mathrm{P} - 3s\,^3\mathrm{D}^a$.

The singlet terms have been put approximately on the same scale by assigning to $3d\,^1\mathrm{D}^a$ a value, 14,000, slightly below that of $3d\,^3\mathrm{D}^a$. A Rydberg formula calculated from the lines $3s\,^1\mathrm{D}^a - 3p\,^1\mathrm{D}^a$ and $3p\,^1\mathrm{D}^a - 4s\,^1\mathrm{D}^a$ gives $3s\,^1\mathrm{D}^a = 101810$, from which $3d\,^1\mathrm{D}^a = 50610$. The difference between this and the adopted value, viz., 36610, should be approximately the difference between the fundamental (^{4}S) and metastable (^{2}D) states of the F^{++} ion. The approximate value derived from an analysis of the F III spectrum (*loc. cit.*) was 38351. We may therefore take the mean value, viz., 37480, as being fairly close to the truth.

Family C.

This family is decidedly weaker than the others, as would be expected. The $3s\,^3\mathrm{P}^b$ terms are close and inverted, and give the $3s\,^3\mathrm{P}^b - 3p\,^3\mathrm{S}^b$ triplet the unusual appearance of having the interval between the strongest pair of lines numerically smaller than that between the weakest pair. The $3d\,^3\mathrm{D}^b$ terms are very faintly represented, but their identification seems to be correct; the apparently abnormal position of $3p\,^3\mathrm{P}_1{}^b - 3d\,^3\mathrm{D}_{21}{}^b$ and intensity of $3p\,^3\mathrm{P}_0{}^b - 3d\,^3\mathrm{D}_1{}^b$ are accounted for by the fact that the observed lines are probably blended with extraneous ones. The $3d\,^3\mathrm{F}^b$ term, however, which, if correctly identified, gives rise to a much stronger group, must be regarded as uncertain. In its favour are the facts that its magnitude is of the expected order, that the group in which it takes part has not unreasonable separations if the $3d\,^3\mathrm{F}^b$ components are close and partially inverted, and that the group is otherwise unaccounted for.

The term values have been assigned on the assumption that the combinations between this family and family A given in Table VI are correctly identified. This is somewhat doubtful, but the terms cannot be far wrong, for the difference of the metastable states, $2p\,^2\mathrm{D}$ and $2p\,^2\mathrm{P}$, of F III is known from observed lines to be equal to 17462 within a few units, while the term values now adopted give a difference of 17530 between the mean values of the $3d$ terms in families B and C. In this connection it may be noted that the ratio of the intervals $2p\,^4\mathrm{S} - 2p\,^2\mathrm{D}$ and $2p\,^2\mathrm{D} - 2p\,^2\mathrm{P}$ in F III, using the amended value for the former given in this paper, is 2·15; the corresponding value for the similar spectrum, O II, is 1·97.

The singlet terms, as in family B, have a wider range of values in the $3p$ group, and a smaller range in the $3d$ group, than the triplets. No suggestion is made as to the $3d\,{}^1F^b$ term since it would combine only with $3p\,{}^1D^b$ and the accuracy of identification of the resulting line could not be confirmed. It should be noted also that the $3p\,{}^1D^b$ and $3p\,{}^1P^b$ terms might be interchanged without violating the combinations found.

An additional, presumably singlet, term denoted by X is suggested. If its combination with $3p\,{}^1D^b$ is real it must be a P term of the magnitude given in the table. This combination, however, is weak and not very exact. If it is accidental, then the X term may be either P or S, and its magnitude may be 45902·1 or − 5111·3.

Comparison of the Spectra F II and O I.

The only spectrum derived from the same electron structure which has been sufficiently worked out for effective comparison with F II is that of the neutral oxygen atom (O I). The chief data concerning this spectrum are given in Fowler's "Report on Series in Line Spectra" (1922), pp. 166–9 (in which the "singlets" and "triplets" are now known to be triplets and quintets, respectively) and in the subsequent work of Hopfield* and Frerichs.† Family A has been more extensively analysed in O I than in F II, but the other families less so. In Table VII are set out all the identified terms of F II with the corresponding O I terms so far as they are known. The data for comparison are not very abundant, but, such as they are, they indicate the usual relations between such pairs of spectra.

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* 'Astrophys. J.,' vol. 59, p. 114 (1924).

† 'Phys. Rev.' vol. 24, p. 1239 (1929).

Table VII.—Terms of F II Compared with those of O I.

Term values.				Intervals between component terms.	
Symbol.	F II.	O I.	Ratio F II/O I.	F II.	O I.
		Family A.			
(*a*) Triplets—					
$2p\ ^3P_2$	280193	109831	2·55	*−344*	*−159*
$^3P_1$	279849	672		*−147*	*− 67*
$^3P_0$	702	605			
$2p'\ ^3P_2$	115395			*−306*	
$^3P_1$	089			*−183*	
$^3P_0$	114906				
$3s\ ^3S_1$	97325·00	33043·3	2·95		
$3p\ ^3P_2$	72485·59	21207·2	3·42	*4·70*	*0·5*
$^3P_1$	490·29	207·7		*−3·00*	
$^3P_0$	487·29				
$3d\ ^3D_3$	48123·14	12350·0	3·90	*2·08*	*0*
$^3D_2$	125·22			*0·80*	
$^3D_1$	126·02				
$4s\ ^3S_1$	43228·57	13612·5	3·18		
$4f\ ^3F_{432}$	25642·9				
(*b*) Quintets—					
$3s\ ^5S_2$	105536·00	36069·0	2·93		
$3p\ ^5P_3$	79549·67	23205·8	3·43	*19·55*	*3·4*
$^5P_2$	569·22	209·2		*11·33*	*2·7*
$^5P_1$	580·55	211·9			

Table VII—(continued).

Term values.				Intervals between component terms.	
Symbol.	F II.	O I.	Ratio F II/O I.	F II.	O I.
Family A—(continued).					
(*b*) Quintets—(contd.).					
$3d\ {}^5D_4$	51032·12	12417·3	4·11	− *0·91*	
${}^5D_3$	031·21			− *1·20*	
${}^5D_2$	030·01			− *0·68*	
${}^5D_1$	029·33			− *0·52*	
${}^5D_0$	028·81				
$4s\ {}^5S_2$	46879·05	14358·5	3·26		
$4f\ {}^5F_{5-1}$	27487·1				
Family B.					
(*a*) Triplets—					
$3s\ {}^3D_3{}^a$	68323·58	8702·91	2·98	−*21·07*	−*12·02*
${}^3D_2{}^a$	302·51	690·89		−*13·03*	− *7·87*
${}^3D_1{}^a$	289·48	683·02			
$3p\ {}^3D_3{}^a$	43994·63			*22·50*	
${}^3D_2{}^a$	44017·13			*2·72*	
${}^3D_1{}^a$	019·85				
$3p\ {}^3F_4{}^a$	42682·29	−3876·09	3·49	− *0·81*	− *6·93*
${}^3F_3{}^a$	681·48	− 883·02		− *0·65*	− *5·68*
${}^3F_2{}^a$	680·83	− 888·70			
$3p\ {}^3P_2{}^a$	40097·10	−3456·43	3·32	−*60·24*	− *3·40*
${}^3P_1{}^a$	036·86	− 459·83		−*26·57*	
${}^3P_0{}^a$	010·29				
$a\ {}^3P_2$	33507·53			*20·12*	
${}^3P_1$	527·65			*7·45*	
${}^3P_0$	535·10				

Table VII—(continued).

Term values.				Intervals between component terms.	
Symbol.	F II.	O I.	Ratio F II/O I.	F II.	O I.
	Family B—(continued).				
(*a*) Triplets—(contd.).					
$3d\ ^3\mathrm{G}_{543}^a$	15695·5				
$3d\ ^3\mathrm{F}_4^a$	15224·29			*7·28*	
$^3\mathrm{F}_3^a$	231·57			*5·51*	
$^3\mathrm{F}_2^a$	237·08				
$3d\ ^3\mathrm{D}_3^a$	14717·50			*−26·04*	
$^3\mathrm{D}_2^a$	691·46			*−18·40*	
$^3\mathrm{D}_1^a$	673·06				
$3d\ ^3\mathrm{S}_1^a$	13829·51				
$3d\ ^3\mathrm{P}_2^a$	13735·93			*−44·85*	
$^3\mathrm{P}_1^a$	691·08			*−17·23*	
$^3\mathrm{P}_0^a$	673·85				
(*b*) Singlets—					
$3s\ ^1\mathrm{D}_2^a$	65200·4				
$3p\ ^1\mathrm{F}_3^a$	44627·1				
$3p\ ^1\mathrm{P}_1^a$	41946·6	*			
$3p\ ^1\mathrm{D}_2^a$	33986·3				
$3d\ ^1\mathrm{D}_2^a$	14000·0†				
$3d\ ^1\mathrm{P}_1^a$	13721·5				
$3d\ ^1\mathrm{F}_3^a$	12869·9				
$4s\ ^1\mathrm{D}_2^a$	9761·8				

* Frerichs (*loc. cit.*) gives −1620·2 for this term, but the evidence is not convincing.

† Assumed value.

Table VII—(continued).

Term values.				Intervals between component terms.	
Symbol.	F II.	O I.	Ratio F II/O I.	F II.	O I.
		Family C.			
(*a*) Triplets—					
$3s\,^3P_2^b$	50118·37	−4072·10	2·89		
$^3P_1^b$	116·76	− 082·54		*− 1·61*	*−10·44*
$^3P_0^b$	114·10	− 088·85		*− 2·66*	*− 6.31*
$3p\,^3S_1^b$	26356·00				
$3p\,^3D_3^b$	24966·90	−17443·83	3·47		
$^3D_2^b$	951·84	− 449·49		*−15·06*	*− 5·66*
$^3D_1^b$	945·24	− 452·90		*− 6·60*	*− 3·41*
$3p\,^3P_2^b$	22376·5				
$^3P_1^b$	400·4			*23·9*	
$^3P_0^b$	415·3			*14·9*	
$3d\,^3F_{432}^b$	1581·4				
$3d\,^3P_2^b$	−3278·7				
$^3P_1^b$	− 244·2			*34·5*	
$^3P_0^b$	− 227·8			*16·4*	
$3d\,^3D_3^b$	−7032·7				
$^3D_2^b$	− 037·4			*− 4·7*	
$^3D_1^b$	− 038·1			*− 0·7*	
(*b*) Singlets—					
$3s\,^1P_1^b$	50435·2				
X	45902·1				
$3p\,^1S_0^b$	22057·4				
$3p\,^1P_1^b$	18733·4				
$3p\,^1D_2^b$	11325·0				
$3d\,^1P_1^b$	−6561·4				
$3d\,^1D_2^b$	−8000·0†				

† Assumed value.

The ratios of term values are of some interest. To make the comparison significant the terms of families B and C have been increased by 37480 and 54942, respectively, in F II, and by 26820 and 40458 in O I. These numbers are the elevations of the respective metastable states of the ions above the ground values. The good agreement of the ratios in all three families for the same orbit of the travelling electron is another indication that the adopted values for the metastable states of F^{++} are of the right order. The ratios for the quintets of family A are very close to those for the corresponding triplets. In each case they steadily approach 4 up to the 3*d* term (the quintet ratio for 3*d* slightly exceeds 4) and then fall again for the 4*s* term. It will be noticed that in O I the 4*s* terms exceed the 3*d*, whereas in F II the 3*d* terms are the larger. Further, the terms of F II do not become negative until the 3*d* level of family C is reached, whereas those of O I become so at the 3*p* level of family B.

The separations of component terms show little relation in the two spectra, beyond agreeing so far as inversion or normality is concerned. The F II separations are usually greater than those of O I—remarkably so in the $3p\ {}^3P^a$ terms—but there are two decided exceptions in $3p\ {}^3F^a$ and $3s\ {}^3P^b$.

Summary.

1. The spectrum of ionised fluorine from the infra-red to the Schumann region has been obtained by passing discharges of appropriate intensity through silicon tetrafluoride, and 469 lines have been obtained and measured.

2. The spectrum has been analysed, and 173 lines have been classified as term-combinations.

3. The analysis has been discussed in relation to theoretical expectations. Terms based on each of the three states corresponding to the normal configuration of the F^{++} ion have been recognised, as well as a triplet and a singlet term apparently arising from other configurations. The approximate value of 38351 for the difference between the ground (^4S) and lower metastable (^2D) states of F^{++}, which was indicated by the F III lines, has consequently been amended to 37480.

4. The existence of quintet, triplet and singlet terms has been established but no intercombinations between them have been found.

5. Term values have been calculated which are all probably close to the true ones. Triplet terms arising from all three states of the F^{++} ion have been

evaluated on the same scale by means of cross-combinations, but the two systems of singlets and the system of quintets have each been given on an independent scale. An ionisation potential of F^+ of 34·6 volts has been deduced.

6. The spectrum has been briefly compared with the similar spectrum, O I.

The Iridescent Colours of Birds and Insects.

By Lord RAYLEIGH, For. Sec. R.S.

(Received May 29, 1930.)

[PLATES 8, 9.]

§ 1. *Introduction.*

It cannot be said that there is yet general agreement as to the origin of the brilliant iridescent colours met with in the animal kingdom, though the balance of opinion attributes them in most if not in all cases to interference of light rather than to any action of pigmentary substances. In the present paper it has been my object to apply methods of investigation which seemed to have been insufficiently exploited by previous workers, in the hope of obtaining further evidence, rather than of supporting any preconceived ideas.

On account of this method of attack the record of work will be subdivided rather according to the form of experiment than according to the animal species investigated.

As regards the general literature, reference may be made to :—

(1) Lord Rayleigh (the late), "On the Optical Character of some Brilliant Animal Colours," 'Phil. Mag.,' vol. 36, p. 98 (1919), or 'Collected Scientific Papers,' vol. 6, p. 584.

(2) Clyde W. Mason, "Structural Colours in Feathers," 'J. Phys. Chemistry,' vol. 27, p. 201 and p. 401 (1923). "Structural Colour in Insects," *ibid.*, vol. 30, p. 383 (1926); vol. 31, p. 321 and p. 1856 (1927).

(3) A. A. Michelson, "Studies in Optics," 'University of Chicago Press,' 1927.

Further detailed references will be given as occasion arises.

§ 2. *Ultra-violet Reflexion.*

Little has been done in the way of examining the ultra-violet reflexion spectrum of brilliantly coloured specimens. Most sources of light are unsuitable, owing to insufficient extension in the ultra-violet, or spectral peculiarities in the source which overlie and obscure the less striking peculiarities due to the coloured reflector. The continuous spectrum of hydrogen is free from these defects. I have used an end-on tube of 8 mm. diameter at 4 mm. pressure and 80 milliamperes current. The source was focussed on the specimen by a quartz lens, and a quartz fluorite achromat was used to form an image of the specimen on the slit of a small quartz spectrograph.*

With the arrangement described, the reflected rays are limited to a fairly definite direction by the small angular aperture of the collimator, and the use of the quartz fluorite achromat ensures that the spectrum is not confused by the overlap of rays from different parts of the specimen.

Various *Morpho* butterflies were examined, very many of them gave similar reflexion, characterised by a fairly well-marked ultra-violet minimum at about λ 2830. Such were *Morpho eugenia*, *M. adonis*, *M. rhetenor* (the species used in making "butterfly jewellery"), *M. menelaus* and *M. sulkowskyi*. As an example the reflexion spectrum of the last named is shown on Plate 8, No. I. In making the exposure a piece of tinplate was arranged to reflect light into the spectrograph at the same time as the specimen, a slight horizontal gap being left vacant between them. Since the tinplate reflects with tolerable uniformity, or at least without marked peculiarities, along the whole spectral range, this comparison reflexion allows us to see at a glance which peculiarities are to be attributed to the source itself, and which to the specimen. In each case the reflexion from the tin is seen above, and that from the specimen below. The same scale of wave-length applies to I, II and III which are placed in register.

The minimum at about λ 2830 was not unforeseen. Assuming that the visual blue colour is due to interference (colour of thin plates) and regarding it as a first order reflexion at, say, λ 4300, then neglecting dispersion there should be a second order reflexion at λ 2150, with an intermediate minimum at λ 2870. This agrees fairly with the observed minimum. In experiments of this kind the minima are better marked than the maxima.

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* This was used because it was at hand, but a small grating instrument would have advantages. The ultra-violet dispersion of the prismatic instrument is too great, making intensity minima in the spectrum less apparent than they might be.

The spectral range of tolerable uniformity in the source and in the plate sensitivity is all too short. Colour-sensitive plates are of little use, because the sensitivity beyond the F line is not uniform, and the peculiarities of the plate dominate everything.

The second maximum (octave reflexion) should be at λ 2150. Actually it is more nearly at λ 2500. This may be due partly to dispersion, which makes the effective optical thickness of the film greater for short waves, but more, I believe, to the rapidly falling intensity of the spectrum in this region.

It is to be remarked that the visual blue colour of *Morpho* is much too strong to be classified as the blue of the first order in Newton's scale, which is a mere bluish tinge. In fact, it is that thickness of film which gives not the blue but the white of the first order which actually reflects most blue. The reconciliation lies in postulating a number of reflecting layers.*

It may be thought that this should make the reflexion fall off more rapidly in the near ultra-violet, and that the octave reflexion should be more localised in the spectrum. It must be admitted that these points remain to be cleared up. We are not bound, however, to assume strict regularity in the spacing of the reflecting planes.

Another species—*Morpho achilles*—differs from the foregoing in that the blue iridescent scales cover only a band across the wing instead of the whole. It differs also in the reflexion spectrum (see Plate 8, No. II). In this case there are two well-marked minima in the ultra-violet region. These are at λ 3750 and λ 2650. These numbers are approximately in the ratio of 7 to 5.

This leads to the following scheme. The fundamental (first order) reflexion is taken to be in the infra-red at wave-length 9400. We have then :—

$\frac{2}{2} \times 9400 = 9400$ Infra-red reflexion.
$\frac{2}{3} \times 9400 = 6260$ Minimum.
$\frac{2}{4} \times 9400 = 4700$ Blue reflexion.
$\frac{2}{5} \times 9400 = 3750$ Photographed minimum.
$\frac{2}{6} \times 9400 = 3130$ Photographed maximum.
$\frac{2}{7} \times 9400 = 2650$ Photographed minimum.

After the minimum at λ 2650 there is another rise of intensity but the failure of the spectrum of the source beyond this makes it impossible to locate the next maximum definitely, or to observe the minimum beyond it.

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* On successive layers in *Morpho*, see Mason, *loc. cit.*, vol. 31, p. 352.

Similar experiments have been made with the coloured moth *Urania ripheus.* The wings show brilliant and varied colours strongly suggestive of thin films. Small uniform pieces were cut from the wing, each representative of one of the colours, and the reflexion spectra were photographed. I was not able to classify the ultra-violet spectra satisfactorily in relation to the visual colour. Thus if we take the first maximum in the photographic region of ordinary plates, this was found at 3640 for a yellow part of the wing, but at 4200 for a green one. On a simple theory we should, of course, expect the shorter photographic wave-length to accompany the green visual reflexion; but on comparing the negatives this is clearly not the case.

Other anomalies have been found. Thus a spectrum of the yellow part of the wing is reproduced in Plate 8, No. III. This differs from I and II in being taken on a colour sensitive (panchromatic) plate; but there is little advantage in this, for as already explained the visual spectrum is dominated by the peculiarities of the plate, which has a marked minimum of sensitivity in the green (see the comparison reflexion from tinplate). We cannot, therefore, attach much importance to the photographic registration of a maximum in the yellow, though in fact it is not incorrect as the visual reflexion is seen golden yellow.

The fairly well-determined maximum at λ 3640 might be regarded as half the fundamental wave-length, which would then be at λ 7280 in the extreme red, or alternatively, it might be one-third of the fundamental, which would then be at λ 10920. The latter supposition accounts best, perhaps, for the colour of the visual reflexion which would correspond to the second order maximum at λ 5460. But this would bring the next minimum to λ 3120. The photographs show the minimum at a definitely shorter wave-length λ 2910, so that neither alternative gave a satisfactory account of the observed result.

Notwithstanding this, I do not seriously doubt that this view of the ultra-violet minima is substantially correct. As already indicated, various circumstances may enter to complicate the detailed application.

§ 3. *Transmission Colour of Morpho Butterflies. Diffraction Spectra by Transmission.*

The view taken above that the blue colour of *Morpho* butterflies is due to thin plates requires that the blue should not be seen by transmission. This is in fact the readiest criterion for distinguishing a pigmentary from an interference colour. H. Onslow has stated* that the scales of *Morpho achilles* are blue both by reflected and transmitted light. This, if correct, would be most important, and would require reconsideration of the whole subject, but I have not been able to verify it. It is always difficult to trace the causes of a discrepancy of this kind, when there is no knowledge of exactly how the experiment was carried out. However, I may say that if the unprepared wing is held up to the window of an ordinary room, with the blue side to the observer, the amount of light that can get through is small, and may well be masked by the blue due to reflexion of the diffuse light of the room. Holding the specimen at the end of a cardboard tube this source of error is avoided, and no blue is seen by transmission, using the open sky as a background.

It is, however, possible to observe diffraction colours through the specimen, and this also might possibly explain Onslow's observation. If a specimen of *Morpho* is mounted in balsam, and held close to the eye, then a localised source, such as a candle some feet off, gives brilliant diffraction spectra.

Morpho rhetenor examined in this way showed spectra somewhat more dispersed than a transparent grating of 14,510 lines to the inch. These spectra were notably brighter in the second order than in the first. The structure of opaque bars responsible for them was readily seen under the microscope with a $\frac{1}{4}$-inch objective. The spacing was about that required. The brightness of the second order would be explained if the opaque bars had one-third of the breadth of the transparent ones,† and this was consistent with what was seen under the microscope. These spectra are not well defined, nor is this to be expected. Each scale is an independent grating, not very uniformly ruled.

It must be emphasised that the diffraction spectra have nothing to do with the blue reflexion. The blue colour disappears when the specimen is mounted in balsam, but the diffraction spectra are best seen with this treatment. As will be seen later, the blue colour is permanently destroyed by exposing the specimen to ultra-violet light, but a specimen so decolourised and mounted in balsam shows the spectra as well as ever. Finally, other species of butterfly, *e.g.*, the ordinary English tortoise shell, which has a real pigmentary colour, show similar spectra.

For observing the spectra, it is desirable, though not really necessary, to bleach the specimen in chlorine before mounting. This improves the transparency.

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* 'Phil. Trans.,' B, vol. 211, p. 37 (1921).

† See Schuster's "Optics," 2nd ed., p. 114.

§ 4. *Change of Colour with Incidence in Iridescent Beetles.*

This is an important criterion of the nature of a coloured reflexion. Observations have been made on beetles showing red colour at normal incidence by the late Lord Rayleigh* and by Prof. A. A. Michelson.† Rayleigh obtained a range of colour from about Fraunhofer's C (λ 6563) at normal incidence to about F (λ 4861) at the most oblique incidences in air, which agreed with his anticipation from the theory of thin plates. Michelson's extreme range was from λ 7000 to λ 5700. The species of beetle was probably not the same, Michelson's being the darker red. Rayleigh's wave-lengths are in the ratio 0·74 and Michelson's in the ratio 0·80. Both are in substantial agreement with the theoretical ratio 0·746 which we get for thin plates, taking $\mu = 1{\cdot}5$.

Rayleigh concluded in favour of thin films. Michelson from this and other experiments concluded against thin films and in favour of surface reflexion, due presumably to high absorption by a pigmentary substance. Rayleigh remarks, however, that "so far as I have seen so great a range cannot be seen in the surface colour of any dye, even with the aid of polarised light."

The range of colour in these experiments was undesirably small; the obliquity within being limited by refraction at the external air-chitin surface. It is particularly desirable to obtain a greater range, since Michelson's experimental curve seems to indicate that a limiting colour had been reached, which would not become *more* and would even become *less* refrangible with higher obliquity. I have modified the experiment to allow of higher obliquities.

The wing case of a beetle *Pelidnota sumptuosa* giving a deep red reflexion at normal incidence was mounted as flat as possible in balsam, in a cavity in an ebonite plate, and covered with a spectacle prism of about 2° angle. With this arrangement we can observe the reflexion at normal or moderately oblique incidences very satisfactorily. It is best to use a restricted area of illumination from a hole in the window shutter. The spectacle prism then throws aside the reflexion from the front surface.

To use oblique incidences, a right-angled prism is added, the hypotenuse being oiled to the surface of the spectacle prism with cedar wood oil, as in using immersion lenses with the microscope. Light can then enter very obliquely to the surface of the insect, by one of the faces of the right-angled prism, and emerges to the eye through the remaining face. With these alternative arrangements we can pass through all the colours of the spectrum, with increasing incidence, from deep red, at normal incidence, to violet at very oblique incidence.

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* *Loc. cit.*, p. 594.

† *Loc. cit.*, p. 170.

A specimen of one of the golden beetles *Anoplognathus viridis*, which is of considerable size, has been similarly mounted under a right-angled prism, after flattening out. In this case too, the colour can be taken right through the spectrum to a deep violet at oblique incidence. The specimen is large enough for projection on a screen, and the change of colour with incidence has been effectively shown to a large audience. The reflexion from a layer of aniline dye spread on glass, showing much the same colour at all angles was similarly demonstrated, and formed a striking contrast.

§ 5. *Transmission Spectra of Iridescent Beetles.*

It was shown some years ago* that the brilliant metallic reflexion of certain beetles showed a spectrum of bands of comparatively closer spacing (of the order of 150 Ångströms) superposed on the broader reflexion band which determines the colour. Reproductions of these spectra were given. Two alternative possibilities were discussed. The bands might be of the same nature as those seen in the surface reflexion of potassium permanganate crystals, described by Stokes; or they might be interference bands. The evidence was held to be strongly in favour of the latter supposition. One of the most telling facts is that the bands shift in a marked way as the specimen is moved in its own plane, even without changing the angle of incidence. In contrast to this the permanganate bands are in definite positions characteristic of this substance, and independent of the angle of incidence over a wide range. Thus the analogy of permanganate reflexion fails, in making no provision for shifting the bands. On the other hand, the position of interference bands depends on the exact spacing of the reflecting planes and some variability over the obviously non-uniform surface of the insect would be expected. The disposition of reflecting planes required to produce these narrower bands superposed upon the general band of coloured reflexion was discussed.

Brilliant reflexion, however caused, must rob the transmitted beam of certain constituents, and give rise to a complementary transmission spectrum. In the case of insects this has not been observed up to the present, so far as I am aware. To observe it the specimen must be made as transparent as possible, so as to avoid absorption or scattering after the reflecting layer has been traversed. This was done by detaching part of the wing case, and immersing it in moist chlorine gas for, say, 24 hours. This treatment often made it easy to see the iridescent reflexion from the under side. In some cases advantage was gained by scraping away from the under side material which has been softened by the action of the gas. The specimen was then mounted as a microscope slide in Canada balsam, with a great gain of transparency. So mounted, the metallic appearance is almost equally well seen from either side. The treatment with chlorine has a remarkable effect in bleaching the brown or black backing present in some species, without injury to the metallic colouring. It was judged, however, that some brownish pigment remained in most cases, thus the transmission colour was not simply the complementary of the reflexion. In one case, *Anoplognathus aureus*, which was exceptionally amenable to treatment, the transmission colour was green, and may be regarded as the complementary of the golden reflexion. Specimens of metallic beetles prepared in this way show transmission spectra of bands, which are, no doubt, complementary to the reflexion bands, though, as might be expected, they show less contrast. The transparent specimen was projected by a low-power microscope objective on to the slit of a small spectrograph, the illumination being provided by a "pointolite" lamp focussed on the specimen. The vertical magnification of the spectra as reproduced on Plate 8 is 24 times. Helium comparison lines have been put on the plate, and a scale of wave-length added in one instance ; it is also applicable to the others. IV, V and VI are different parts of a specimen of *Anoplognathus aureus*, on a panchromatic plate. VII is the same on a kryptocyanine plate, sensitive to the extreme red. VIII is *Callodus parvulus* (another golden beetle) on a panchromatic.

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* 'Roy. Soc. Proc.,' A, vol. 103, p. 233 (1923).

In all these the sinuosity of the transmission bands is very obvious as we pass across the specimen.

In these beetles the bands are exceptionally distinct. In others such as *Anoplognathus viridis* and *Mimela lei* they are less so, though still fairly conspicuous. In some other iridescent beetles I have not been able to detect them at all.

The ultra-violet is not transmitted beyond about λ 3100, even with chlorine-treated specimens mounted between quartz plates in glycerine. This want of transparency probably explains why an octave reflexion at about λ 2800 is not observable in any of the metallic beetles that I have tried. An absorbing layer may be supposed to overlie the reflecting layer.

§ 6. *Action of Chlorine Gas on Animal Colours.*

These experiments are easy, and often give instructive results. The specimen is simply immersed in a jar of moist gas. By using chlorine gas instead of hypochlorite we avoid any change of colour or appearance due to wetting. Moreover, the gas may be trusted to penetrate the interstices of the specimen.

The blue colour of *Morpho* butterflies, or of the paler English blue butterflies, is not fundamentally affected by keeping them in chlorine for several days. If there is an opaque black backing as in *Morpho rhetenor*, and most other species, this is bleached by the treatment, and the richness of the blue reflexion is lost. This is not surprising, as the colours of thin films show best on a black background (*cf.* oil films on a tarred road). No doubt the black backing is there for that reason. The blue colour of *Morpho rhetenor* after bleaching resembles the natural appearance of *Morpho sulkowskyi*, a species which has no black backing. After a week or two in chlorine the material disintegrates altogether, and the colour is lost.

In *Urania ripheus* too, colour survives when the background is completely bleached by chlorine. On immersion the tints change; those portions which show the plum coloured "tint of passage" rapidly change over into blue, and further changes occur. After about 30 hours varied colours remain on the bleached background, much impoverished just as in the case of *Morpho*. Their whole behaviour seems unmistakably that of interference tints.

The colours of the golden beetles are very resistant to chlorine. The wing cases are conveniently treated in this way to make them transparent (see above, p. 631), but the iridescent colour is unaffected unless the action is prolonged for a week or two. In that case the material becomes disintegrated, and goes quite white.

In marked contrast to all the cases above mentioned is the action of chlorine on the red pigmentary colours of butterflies and on all kinds of coloured feathers. The colour is completely discharged, and in most cases quite quickly.

The various yellow green and blue parrots' feathers completely lose their colour after an hour in moist chlorine. Where both blue and green are present, the two colours fade away *pari passu*. A brown background remains, but is bleached after about 24 hours' treatment.

The colours of the peacock's "eye" (coloured pattern in the tail feather) are quickly affected. After a few minutes the straggling outer parts become reddish and then dull brown, without a trace of the metallic colour. The blue-green zone (innermost but one) is considerably more resistant, but after an hour or two this likewise becomes a dull brown. The general pattern remains discernible, however, even when the colours are gone.

The blue colour of the jay's feather, which is located in the barbs and not in the barbules, disappears in about 1 hour, leaving brown.

So far as the chlorine experiments alone are concerned, we may sum up by saying that all feathers are easily decolourised by this agent, no distinction being apparent between "metallic" colours and others; nor, if a different classification is used, between blues and reds.

In butterflies, blue colour is resistant to chlorine, and so are the varied colours of *Urania ripheus* ranging from red to blue. On the other hand, the various red and yellow colours of an undoubtedly pigmentary character are easily discharged by moist chlorine.

In metallic beetles, the colour is resistant to chlorine.

§ 7. *Fading of Colours in the Light-visual and Ultra-violet.*

It is known that many animal colours are unstable in the sunlight, and this is a source of anxiety to the curators of zoological museums, who have probably been more anxious to prevent the fading than to examine it. Mason* has examined the fading of various kinds of feathers. His conclusion is that the pigmentary yellow of feathers is easily faded, but that the blue, which he regards as structural in all cases, is unaffected. Green feathers became blue in the equivalent of 30-60 hours of direct sunshine. This is attributed to the fading of a yellow overlying layer.

Nothing seems to have been published with regard to the action of ultra-violet light, except some preliminary notes of my own.† Strong ultra-violet sources are in general far more potent than sunlight in causing chemical changes, and it was hoped that perhaps this might be the basis of an unambiguous method of distinguishing structural from pigmentary colours. Unfortunately, such has not proved to be the case.

Various mercury arcs in quartz were used. A specimen of *Morpho rhetenor* exposed close to the lamp for 10 minutes showed perceptible fading, when compared with a screened area on the same specimen. The blue tint of every scale was of diminished intensity, but there was no tendency to a change of tint. After a few hours the specimen was completely decolourised, only the black background remaining. The same change can be induced by direct sunlight. Exposure for a month to the sky in summer produces a very marked effect, which, however, is far from complete.

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* 'J. Phys. Chem.,' vol. 27, p. 249 (1923). He speaks of a "fadeometer" apparently an arrangement for concentrating sunshine.

† 'Nature,' vol. 121, p. 827 (1928); vol. 122, p. 167 (1928).

There is marked contrast between the effect of chlorine and of light. Chlorine leaves the blue colour but destroys the black background. Ultra-violet light destroys the blue but leaves the black. The various colours of *Urania ripheus* are affected by ultra-violet light in a way which, to naked eye examination, appears similar to the effect on *Morpho.* That is to say, the colour fades without much change of tint. Green remains green, and yellow remains yellow, until the colour finally disappears, leaving a drab background.

But under a lens a distinction appears, for whereas a partially faded *Morpho* shows diminished intensity in every scale, partially faded *Urania* shows some scales apparently as bright as at first, while others have lost all colour. Indeed, it is not easy to recognise the presence of small areas of intermediate brilliancy. There are complications connected with the direction of incidence, the fading appearing much more conspicuous under certain aspects.

The appearance suggests that the colour disappears by a kind of *débâcle*, when once the change has set in. There is room for a further careful investigation, arrangements being made to observe single scales while they are caused to fade.

Parrot's feathers have, in my experience, shown a simple behaviour, differing from Mason's results. A feather, part of which was green and part blue, was exposed about 1 cm. away from a vacuum lamp, and below it, to minimise heating. After 8 hours the blue and green were both very much less brilliant, without change of tint. In particular the green did not show any tendency to become blue, as in Mason's experiments, and the blue faded as easily as the green, and as easily or nearly as easily as a red feather in another experiment. Both the green and the blue portions were tending to become black, but the experiment was not pushed to the point of discharging the original colours altogether. I do not doubt that with an exposure two or three times longer this would be the result.

The colour-changes produced by light in peacock's feathers are far more complex, and no attempt will be made to describe them exhaustively. For convenience of reference I speak of colour zones in the peacock's "eye," numbering them from the inside. The colours depend a good deal on the angle of incidence, and display less apparent variety and complexity at oblique than at normal incidence. For that reason oblique incidence should be used in identifying the zones from an actual specimen. My descriptions refer to a large tail feather showing the "eye" in its most complete development.

For normal incidence the observer should stand with his back to the window and hold the specimen in front of his eyes. For oblique incidence the feather is held horizontally at a lower level than the eyes, between the observer and the window.

The colour scheme may then be roughly described as follows :—

Zone.	Normal incidence.	Oblique incidence.
1 (centre)	Dark blue	Black.
2	Bright green	Bright blue.
3	Olive yellow	Reddish brown.
4 (includes straggling outer parts)	Complex. Includes yellow purple and bronze sub-zones	Green.

After exposure to a mercury lamp for a few hours or to direct sunlight for the whole available sunshine of our English summer, the colours are considerably altered. It is convenient to screen half the feather for comparison.

The altered colour scheme is as follows :—

Zone.	Normal incidence.	Oblique incidence.
1 (centre)	Black	Black.
2	Blue	Violet.
3	Brownish purple	Dull green.
4 (includes straggling outer parts)	Still complex. Greenish on the whole	Bluish green.

In most parts of the feather the effect of obliquity is to make the general colour effect as judged by the eye more refrangible, though the third zone is an exception.

Prolonged exposure to light also makes the general colour effect more refrangible, whether the comparison of exposed and unexposed halves of the feather is at normal or at oblique incidence.

Although the effects of exposure to light and of increased obliquity are thus broadly similar the comparison cannot be pushed into minute details.

The bluish colour seen in the straggling outer parts of the exposed feather constitutes a striking change, and is best seen at considerable obliquity.

As exposure is continued the tendency is for the colours to become duller as well as more refrangible, and the ultimate result, never fully reached in these experiments, would doubtless be to destroy all bright colour, leaving the feather dark and dull, but with the zones still distinguishable.

For the changes as seen at nearly normal incidence see Plate 9. The photograph in blue light was taken on an ordinary plate, by the light of the blue mercury line λ 4358, isolated by a suitable filter. The other was on a panchromatic plate, using the light of an ordinary ruby photographic bulb.

These approximately monochromatic photographs are in some ways more instructive than the complex colour effects seen in white light.

By blue light it is noticeable that the first zone is made less reflective by exposure, and the third zone more reflective. There are complex changes in the fourth zone, upon which I do not enter.

But the photograph by red light is the most striking. Here the second zone is made much more reflective by exposure and the third zone much less reflective. The complex fourth zone is for the most part made more reflective also.

Considering the two photographs together the most distinctive changes are seen in the third zone, which, by exposure, becomes more reflective for blue light and less for red. This is in agreement with the result of visual examination that exposure makes the general colour effect in each zone more refrangible, but, as we shall see later, this statement does not cover the whole ground.

The photographs are useful for illustration, but they offer no particular advantage when the original specimen is at hand, since this may be examined in sunlight, holding an appropriate colour filter over the eye. The result of such an examination at normal incidence was as follows: the effect of exposure is stated.

Filter.	1st zone.	2nd zone.	3rd zone.
Violet. Wratten, No. 76	Darker	Doubtful	Brighter.
Blue. Wratten, No. 47	Darker	Doubtful	Brighter.
Green. Wratten, No. 74	Doubtful	Darker	Darker.
Red. Wratten, No. 29	Doubtful	Brighter	Darker
Deep red. Wratten, No. 70	Doubtful	Brighter	Much darker.

This confirms the photographic results, with more subdivision of the spectrum.

Both the photographs and the visual use of colour screens show that the second zone reflects more red light than it did before exposure, though its visual effect is changed from bright green to blue. To get more definite information the image of a slit illuminated with white light was thrown upon the feather, and this image was examined with a grating or direct vision prism held over the eye. It was viewed in a direction roughly that of specular reflexion.

In the second zone of the unexposed part of the feather it was found that at normal incidence the reflexion was concentrated in the green of the spectrum. Increasing the incidence caused this maximum to move towards the blue, and a distinct minimum became apparent with revived reflexion in the red.

The effect of exposure of the second zone to ultra-violet light is similar. If we compare the spectra of the exposed and unexposed parts which is readily done if part of the image of the slit falls on each, we find that at normal incidence the exposed part has its green maximum shifted to the blue, and a red reflexion comes in, with intervening minimum.

Spectroscopic examination of the other zones did not give equally distinctive results. There is room, however, for a careful examination by spectrophotometry, which might yield important information.

It is suspected that the changes induced by exposure to ultra-violet light are not limited to the actual period of exposure, but progress afterwards. This requires further verification.

It is certain, however, that wetting has a remarkable effect on an exposed feather. This was first noticed when the rain had been inadvertently allowed to fall on a specimen which was being exposed to sunshine. It is, of course, well known that an ordinary unprepared feather shows marked temporary colour changes while actually wet. The effect here described is quite distinct from this.

The whole feather is exposed to the mercury lamp, a similar unexposed feather being reserved for comparison. Half of the exposed feather is then wetted, the other half being carefully kept dry. When the whole is dry again, it is found that the temporary wetting has developed a permanent difference between the two halves. It is difficult to give a satisfactory verbal description. A specimen after 14 hours' exposure at 15 cm. distance, was wetted on one side of the stalk and allowed to dry. It was examined at oblique incidence. As described above the colours of the various zones had been made more refrangible by the exposure. The effect of temporary wetting and drying was to restore the colours to a considerable extent, and thus to neutralise the effect of the exposure. This was particularly clear in the third zone, which recovered its original reddish-brown colour almost completely.

In another exposed similarly for 76½ hours the original colours had become very dull. In this case the effect of wetting with subsequent drying was to make them duller still, without marked change in the tint of such colour as remained.

§ 8. *Discussion of the Action of Light and of Chlorine.*

As we have seen, the colours which are stable to chlorine are not in all cases stable to light. We might, however, propose tentatively the view that easy destruction by either one of these agents reveals the presence of a pigment (which might act either by absorption or by surface reflexion). This view is contradicted by the cases of *Morpho rhetenor* and *Urania ripheus*. Here the colour, and hence the pigment if any, survives chlorine. But if we mount the specimen in balsam, after chlorine treatment, it is found to become practically *colourless and transparent*. Hence it is proved to demonstration that there is no pigment.

We cannot then regard fading by light as indicating a pigment. Can we assume that rapid loss of colour in chlorine indicates a pigment? This view is much more plausible, but upon the whole I am not able to adopt it. Peacock's feathers readily lose their colour in chlorine, but Mallock* has found that the colours of these feathers disappear under pressure, and in this fact he finds conclusive proof that they are not due to any kind of pigment. I do not know of any answer to this argument.

If, however, we cannot infer anything from *instability* in chlorine, or to light, we may perhaps regard *stability* under these agents as a proof that no pigment is concerned. The colours of *Urania* and *Morpho* are stable to chlorine. The colours of metallic beetles are stable both to light and to chlorine. On other grounds there is no objection, and much in favour of regarding all these as interference colours.

We have next to consider the other class of cases, where chlorine or light have a definitely destructive action on the colours. As we have seen, this does not afford a definite criterion as to their origin. It has hitherto been supposed that all ordinary blue feathers,† and probably also feathers showing iridescent colours, were completely stable towards light, and this seemed an important confirmation of the view that they were structure colours. This particular argument now fails, since peacock's feathers and blue (as well as green and red) parrot's feathers are found to be unstable under the mercury lamp. Unfortunately it has not so far been practicable to get rid of the black backing and to examine these colours by transmission. However, Mallock's pressure experiment seems decisive for structure colours in the case of the peacock at least. Accordingly, we are apparently driven to assume that in this case, and also in the cases of *Morpho* and *Urania*, the action of light is to destroy a colour-producing structure, probably by photochemical decomposition of the chemical substances of which the structure is built.

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* 'Proc. Zoological Soc.,' p. 225 (1921).

† Mason, *loc. cit.*, vol. 27, p. 249.

We have seen that in the case of peacock's feathers the initial effect of light is generally to make the colour more refrangible, thus to contract the scale of the structure to which (on the interference theory) it is due. But this is not a complete account of what happens, for at the same time the brightness diminishes. In *Morpho* and *Urania* on the other hand we have diminished reflexion without much change of tint. In these cases too the view taken is that the material of an interference structure is destroyed, rather than a pigment. The case of the peacock's feather is most in accordance with expectation. If we take a thin film of cellulose acetate on glass, for example, and expose it to the mercury lamp with part screened, we find that a red part, *e.g.*, may pass over into blue as the result, no doubt, of chemical changes* which cause the interference tint to move progressively along Newton's scale.

As we have seen nothing of this kind is observed when *Morpho* and *Urania* are faded by the mercury lamp. The difference between these cases and the peacock remains unexplained.

The faded and unfaded parts of a *Morpho* wing were tested for fluorescence under ultra-violet light, using a nickel oxide glass filter. A marked fluorescence was to be seen in the original blue wing, which was entirely absent in the faded part. This may be considered to prove that the fading is accompanied by the destruction of a fluorescent substance. If this experiment stood alone, it would be tempting to assume that the fluorescent substance was a pigment, acting either by absorption or by selective reflexion. The apparently conclusive arguments against a pigment remain unshaken however, and it is natural to fall back on the view that what is destroyed is a colourless fluorescent body which builds the interference structure.

Peacock's feathers are not fluorescent, either originally or after exposure.

§ 9. *Summary.*

The reflexion spectra of various brilliantly coloured insects are examined in the ultra-violet. *Morpho* butterflies and *Urania* moths are found to show ultra-violet maxima in general agreement with the theory of interference. In

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* See an experiment of this kind De Vore, Pfund and Cofman, 'J. Phys. Chemistry,' vol. 33, p. 1836 (1929). They experimented with nitrocellulose. I have used cellulose acetate.

Morpho achilles the positions of the ultra-violet maxima indicate that the blue colour is due to a reflexion of the second order. Spectra are reproduced.

Contrary to some previous accounts, no *Morpho* butterflies are found to show their blue colour by transmission. They do show brilliant diffraction spectra by transmission, when suitably mounted in balsam, but these have nothing to do with the blue reflexion.

Iridescent beetles showing a deep red colour at normal incidence may be made to pass through all the colours of the spectrum to violet, provided that arrangements are made to annul refraction at the air-chitin surface, so as to obtain very oblique incidence within. This is in sharp contrast to the surface reflexion of aniline dyes, which do not show much change of colour with incidence.

Some of the golden beetles show transmission spectra of bands corresponding to the reflexion spectra formerly described. These bands vary continuously in position with the part of the specimen examined. It seems impossible to interpret this reasonably except on the theory of interference, for the transmission bands of chemical substances do not vary from one sample to another. The spectra are reproduced.

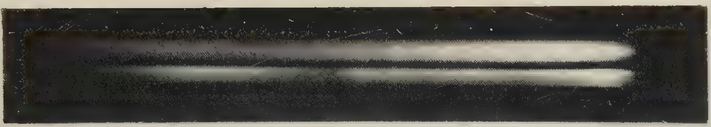
Moist chlorine gas does not destroy the colours of *Morpho* or of *Urania* though the black background is bleached. Nor does chlorine decolourise the metallic beetles. The colours of all kinds of feathers, however, are rapidly discharged.

Peacock's feathers undergo a progressive change of colour in ultra-violet light or long-continued sunlight. Generally speaking, the colours become more refrangible and less brilliant.

Other feathers (*e.g.*, parrot) even when blue are slowly decolourised without change of refrangibility. *Morpho* butterflies and *Urania* also lose colour without change of refrangibility.

Although, *prima facie*, fading under light or chlorine in these cases would seem to favour the idea of a pigment, it is not considered that this view can be maintained. The fading must rather be attributed to the breaking down of an interference structure. It remains unexplained why the progressive changes of tint seen in peacock's feathers are not seen in the other cases examined.

The generalisation seems to hold good, however, that colours which are stable in chlorine are certainly *not* due to pigment.



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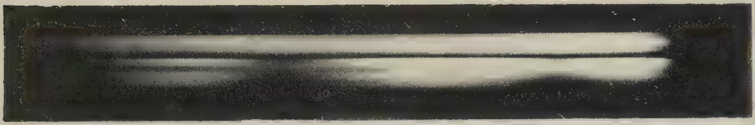

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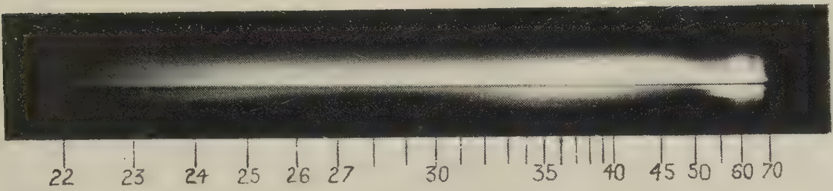
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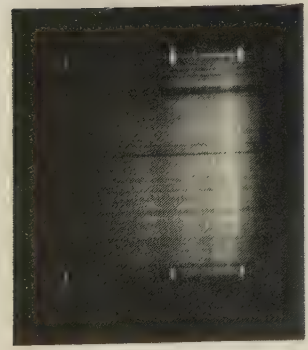
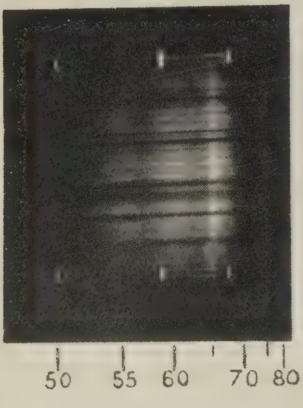
70

III

IV

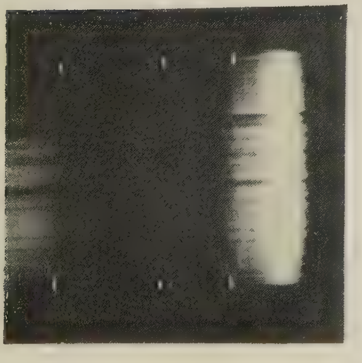


V

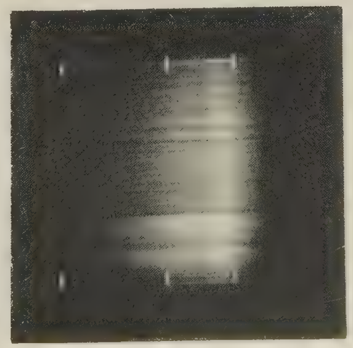

50
55
60
70
80

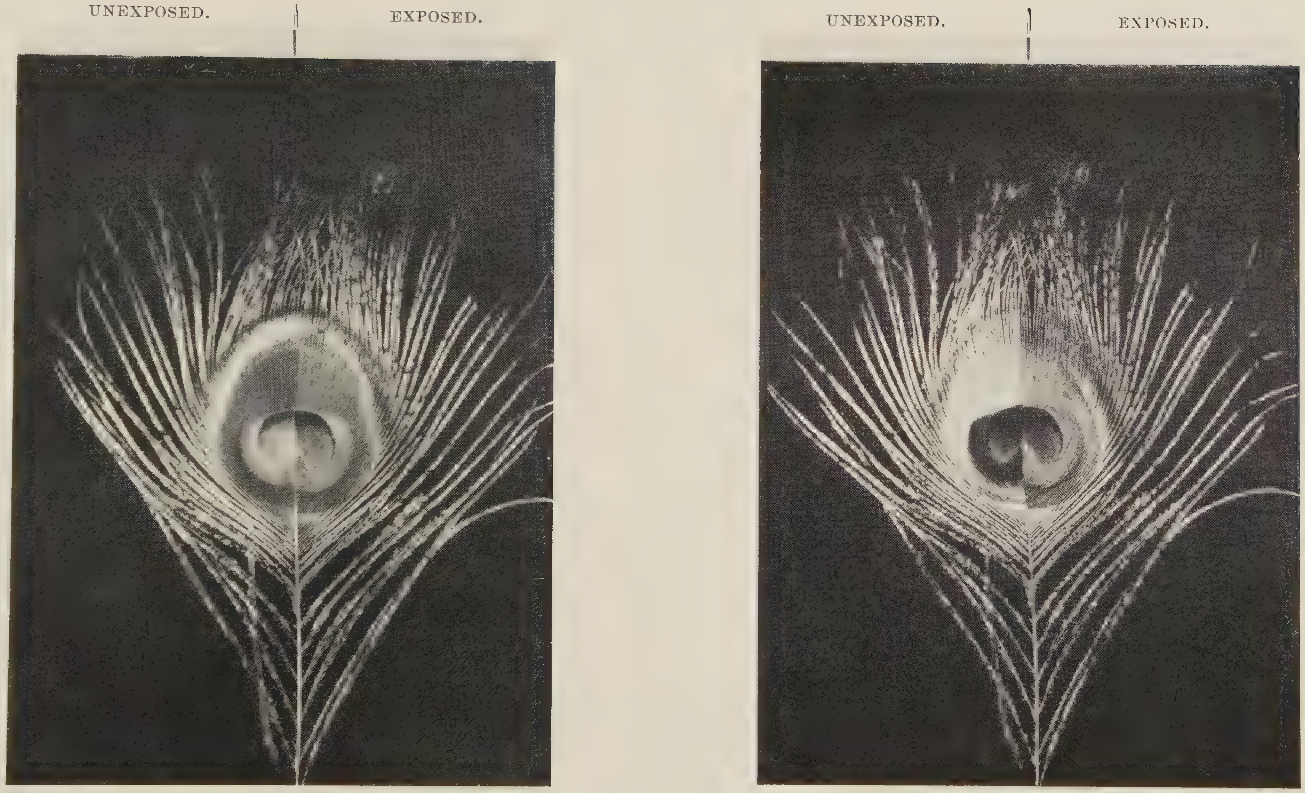
VI

VII



VIII




UNEXPOSED.
EXPOSED.
UNEXPOSED.
EXPOSED.

IN BLUE LIGHT.

IN RED LIGHT.

Peacock's feather at normal incidence. Right half of feather exposed to mercury lamp for some hours.

DESCRIPTION OF PLATES.

Plate 8.

I, II, III are reflexion spectra. The scale of wave-lengths applies to all.

I. Tin plate above. *Morpho sulkowskyi* below. Ordinary plate.

II. Tin plate above. *Morpho achilles* below. Ordinary plate.

III. Tin plate above. *Urania ripheus* below. Panchromatic plate.

IV to VIII inclusive are transmission spectra, with helium comparison lines above and below. The scale of wave-length below V applies to all.

IV, V, VI. *Anoplognathus aureus* panchromatic plate.

VII. The same. Kryptocyanine plate.

VIII. *Callodus parvulus*. Panchromatic plate.

Plate 9.

Peacock's feather at normal incidence. Right half of feather exposed to mercury lamp for some hours.

A Camera for Electron Diffraction.

By G. P. Thomson, M.A., Professor in the University of Aberdeen, and
C. G. Fraser.

(Communicated by Sir Joseph Thomson, F.R.S.—Received May 6, 1930.)

[Plate 10.]

The apparatus described in this paper, which will be called for shortness an electron camera, is intended to study the diffraction patterns formed by the reflection of cathode rays from crystalline surfaces. It differs from the original apparatus used by Davisson and Germer for this purpose in that the method of detection is photographic instead of electrical, and that the energy of the electrons is much greater, being at least 6000 volts (more usually 30,000) instead of about 300. In consequence of the much greater penetrating power of these fast rays it is not necessary to use an elaborate vacuum technique.

The principle of the apparatus is that a narrow beam of cathode rays generated in a gas-filled discharge tube is selected by passing through two fine pin-holes and then strikes the crystalline target, where it is diffracted into divergent beams which ultimately strike a photographic plate.

The Apparatus.—The camera may be considered as consisting of three main parts :—

I.—The camera proper, including the plate holder A and the main tube E.

II.—The crystal chamber F.

III.—The discharge tube M (see fig. 1, Plate 10).

The Plate Chamber A.—This is a built-up brass box containing the plate in its carrier, to which is fixed a rack which can move through the top of the box into the glass tube B, fig. 1. A pinion, controlled by the handle C, is in mesh with the rack, the shaft passing through the front plate (12, fig. 4) by way of a conical ground joint. This arrangement serves to raise or lower the plate carrier, and the exact position is seen at any instant by means of the index placed in the glass tube B, fig. 1. The front plate has on it at its lower end a fluorescent screen (Willemite), 1, fig. 4, for visual examination of the diffraction pattern, and at the upper end a door, sealed in with Everett wax, which may be removed to allow the photographic plate 17 to be put into the carrier.

The Main Tube E.—The ebonite block D serves to insulate the plate chamber from the main tube E, which is connected direct to the crystal chamber F. The object of D was to allow a back potential to be applied to the plate and grid (16, fig. 4). The latter is of about 3 mm. mesh and is mounted in an aluminium tube projecting into E and in metallic contact with the plate chamber. It was hoped that, by stopping those of the rays which had lost much energy by inelastic collisions, the proportion of regularly diffracted rays to diffuse background would be increased. In practice, using 6000 volts on the discharge and a back potential of 2000–4000 volts on the grid, the diffraction pattern was found to lose in clearness, and at last become invisible, owing partly to the deviation caused by the grid, and partly to the lack of photographic contrast given by slow electrons. This feature will therefore be omitted from future instruments. The rectangular network of lines on Plate 11 is the shadow of this grid.

The Crystal Chamber.—This consists of a circular brass box having a glass window (1, fig. 2) at its lower end. Through the top of the box passes a large conical ground joint (2, fig. 2) carrying a slide (3, figs. 2 and 4) which serves to impart a to-and-fro motion to the crystal holder (4, figs. 2 and 4). This slide is moved by a rack and pinion controlled by the handle H (figs. 1 and 2) through a secondary ground joint (5, fig. 2). The handle is arranged to work against an adjustable stop so that the crystal holder may be returned to any predetermined position. On the top of the main ground joint is fixed a degree plate moving past an indicator with adjustable zero (6, fig. 2) which serves to show the angle at which the face of the crystal or target (8, figs. 2 and 4) is held to the incident rays. This angle can be read through the lens (9, fig. 2).

In order to rotate the target in the plane of its surface, it is mounted in a conical bearing, and moved by a control I (figs. 1 and 2) through a ground joint and universal telescopic shaft 7 (figs. 2 and 4). The inside of the crystal

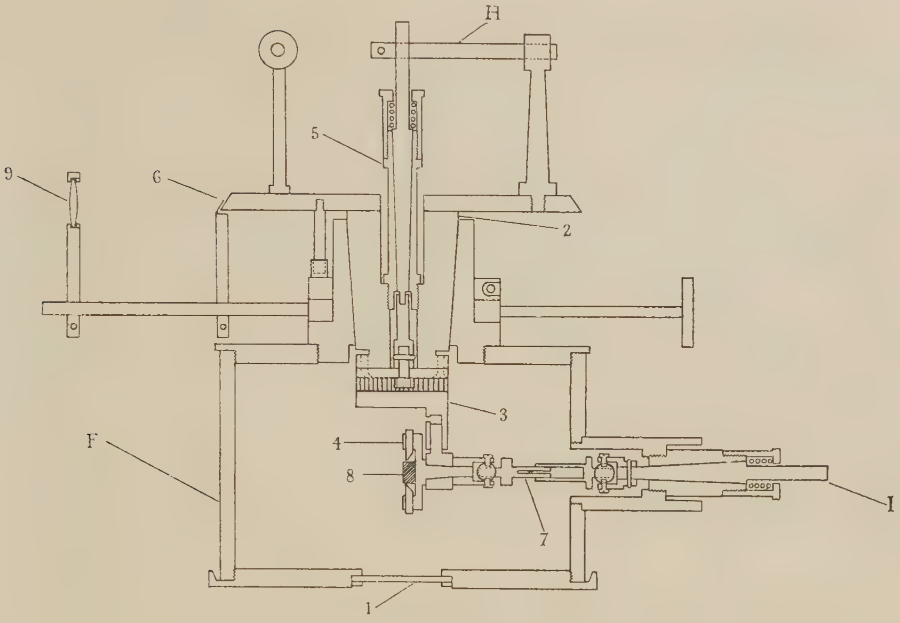

H
5
9
6
2
3
4
8
F
7
I
1

Fig. 2.

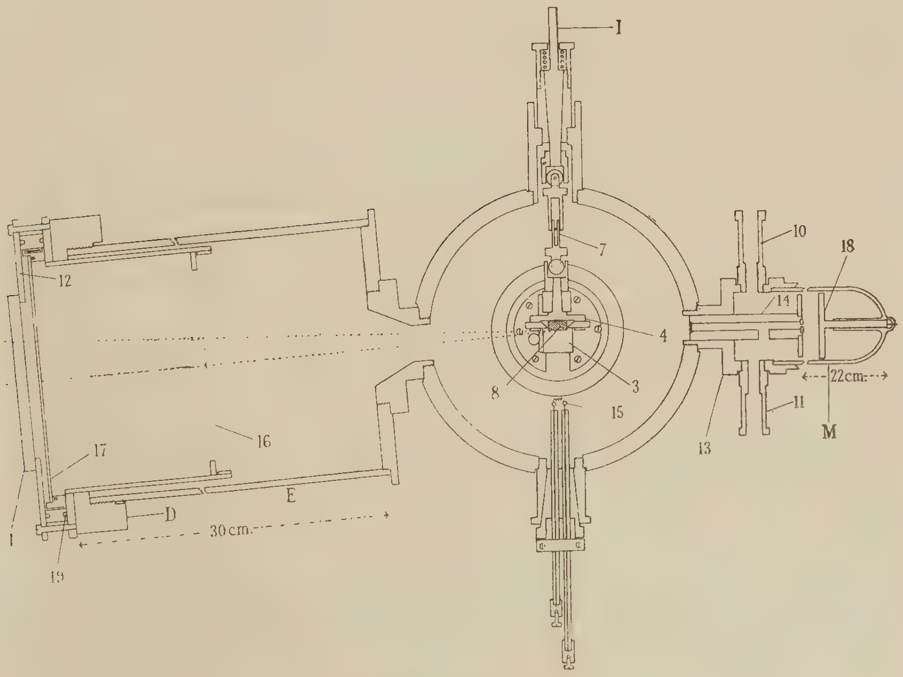

I
7
10
18
12
14
4
8
3
22cm.
15
M
11
13
16
17
E
D
30 cm.
1
19

Fig. 4.

chamber is shown in fig. 3. Besides the parts already described there are two devices for heating the surface of the target. One (15, fig. 4) is a hot filament, insulated by quartz tubes from the chamber, which can be used to bombard the target with electrons. The other, omitted from figs. 2 and 4 for clearness, consists of a helix X (fig. 3) of nickel chrome wire mounted on a holder, which can be rotated in a ground joint through 90° by means of the handle K, so as to bring it in front of the target. The handle K also serves as one terminal for the coil. The other end of the coil is connected to a copper clamp which is round a porcelain insulator on the rod controlled by K, and this clamp is arranged to make contact with the copper arm leading to the terminal L only when the heater has been raised in front of the crystal. The action of raising the heater, therefore, serves to switch on the current. Though this device worked well, the heat available by radiation was not very intense. A better plan, which has been tried, is to use as target the outer surface of a nickel capsule which can, of course, be covered with a deposit of any other metal to be tested. Inside the capsule is a heating coil wound between quartz rods, the leads to which pass through K and L as described above. The capsule is, of course, mounted on the usual target holder, the leads hanging loose in the chamber. This enables the surface to be kept at a red heat while the photograph is being taken, and would be valuable if the effect of gas layers became important; so far these have not obtruded themselves and the device has been little used.

The Discharge Tube.—A brass socket (7, fig. 4) serves to carry the discharge tube M and has mounted in it the aluminium anode (14, fig. 4) This anode has inserted in it at each end an aluminium disc having a hole 0·15 mm. diameter in its centre, through which passes the electron beam from the cathode (18). The side tube 10 is the inlet for gas to the discharge, and the tube 11 connects to the main tube E (fig. 1) and to the pump. The gas used for the discharge was usually hydrogen generated by electrolysis, dried in a gas chamber by P_2O_5, and admitted to the discharge tube through an adjustable leak. A three-stage steel Gaede diffusion pump sucked the gas through a mercury trap P from the tube E, the taps between being fully open. The tap Q was kept partially shut, so that the pressure in the discharge tube (of the order of 5/1000 mm.) was much greater than in the camera. The trap R leads to the McLeod gauge, which was used chiefly as an indicator of leaks; owing to the flow of gas through the holes in the anode it does not give a fair measure of the pressure in the camera.

Magnetic Adjustment.—The whole apparatus is mounted in a brass ring which can turn in two bearings N (fig. 1) fitted on top of the wooden stand. With this arrangement it is possible to set the camera so that the path of the beam is in the direction of the earth's magnetic field, and the beam is therefore not deviated.

Joints.—The joints of the plate holder were made airtight by picein run into grooves (19, fig. 4) machined in the brass frame. The screwed joints were all tinned, and put together with the tin molten. A fillet of wax was run outside for additional security and these joints have given no trouble. The ground joints were very carefully fitted in the first instance. The big joint has had to be regreased once in 8 months' working, but otherwise they have caused no trouble.

Discharge.—The discharge was generally produced by an induction coil rectified by a Kinotron valve. This gives a surprisingly homogeneous beam of electrons, especially if a couple of Leyden jars are connected in parallel with the discharge. For lower voltages (about 6000) an Evershed and Vignolles direct current generator was used.

Method of Working.—After a target has been fitted, the apparatus is pumped out with solid CO_2 on the traps to prevent the diffusion of mercury vapour from the pump and McLeod gauge ; the stream of gas through the apparatus must then be adjusted so that the pressure in the discharge tube is suited to the energy of ray desired. It is then desirable to test the sharpness of the beam by withdrawing the target by the rack and pinion. A brilliant spot will appear on the willemite screen, generally surrounded by a bright ring. This is an optical effect due to reflection of light within the thickness of the glass plate carrying the willemite. It always occurs when the spot is bright, and has, of course, no connection with electron diffraction. If the beam is satisfactory, the target is brought back till it cuts off nearly the whole of the beam. Scattered rays will illuminate one half of the field, the other being shielded by the target, and spots or diffraction rings may be seen. The angle of incidence of the target, and its aximuth, are then adjusted by turning the large ground joint and the side handle, till the brightness of the pattern is a maximum. The movement in azimuth is of secondary importance for polycrystalline targets, but is useful as a means of trying different parts of the surface and so finding the most effective. Rings were observed on the willemite screen in the early experiments of electron diffraction,* but with the new apparatus they are much brighter with a good target. The photograph, however, is always clearer, and often gives easily measurable rings when the screen gives no certain indications. When the target is adjusted the photograph is taken by quickly lowering the plate with the discharge off, and then switching it on for the required time. This varies, of course, with the intensity but is of the order of 10 seconds for 30,000-volt rays with the coil used. For 6000-volt rays it is about 5 minutes, though the difference in brightness on the screen is not very great. The plates used were Paget Process Plates.

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* 'Roy. Soc. Proc.,' A, vol. 117, p. 603 (1928).

Theory.

Selective reflection will occur if the rays strike a set of crystal planes of spacing d at the glancing angle θ given by

$$2d \sin \theta = n\lambda = nh/mv, \tag{1}$$

where n is an integer and mv is the momentum of the electron. The angle θ is determined by measuring x, the distance on the photographic plate between the place at which the beam would have struck if there had been no target, and the diffracted spot or ring. Then $\tan 2\theta = x/\mathrm{L}$, where L is the perpendicular distance from the target to the photographic plate. Since θ is small ($< 4°$) we have

$$d/n = \frac{\mathrm{L} \, . \, h}{mv \, . \, x} = \frac{12{\cdot}25 \, . \, \mathrm{L}}{x\sqrt{\mathrm{P}}\,(1 + \mathrm{P}e/1200mc^2)}, \tag{2}$$

where P is the energy of the electrons in volts and d is in Ångstroms (10^{-8} cm.). The factor in brackets in the denominator is a correction due to relativity, which never exceeded $2\frac{1}{2}$ per cent. in this work and is generally negligible.

A correction is needed to the above if there is refraction of the rays at the crystal surface. It can be shown that if the refracting surface is parallel to the reflecting planes equation (2) is modified to

$$d/n = \frac{12{\cdot}25\mathrm{L}\sqrt{1 - 4d^2\Phi/150n^2}}{x\sqrt{\mathrm{P}}\,(1 + \mathrm{P}e/1200mc^2)},$$

where Φ is the "inner" potential of the crystal in volts, which is related to the refractive index for electrons μ by the equation $\mu = \sqrt{1 + \Phi/\mathrm{P}}$. This correction may be very important, but only in the case stated above when reflecting and refracting surfaces are parallel. Otherwise it is negligible.

With a single crystal selective reflection, as in the case of X-rays, will only occur for special settings of the crystal or special wave-lengths of the electrons. In such cases a reflected spot should appear on the plate. If the target is a mass of small crystals we should expect to get portions of concentric circles ("rings") covering that portion of the plate not shielded from the rays by the target. The radii, when substituted for x in equation 2, give the crystal spacings responsible for the various rings. Specimens of rings are shown in Plate 11, figs. 1, 2 and 3 of the following paper.*

Experimental Errors.

Zero Error.—In order to use the results of experiments with the electron camera to investigate the structure of the target (see next paper) it is necessary to know the zero of the plate, that is the place where the rays would have hit it but for the interposition of the target. Owing to the very small angle at which the target is set to the incident beam a portion of the latter often escapes past the edge (see Plate 11, figs. 1, 2 and 3). One is not, however, justified in taking this mark as the zero, for it is not made by the centre of the beam. Two means of finding the true centre are available; it can be found from the circular arcs, or we can withdraw the crystal by the rack and pinion and then take a short exposure of the undeflected beam. In the latter case the beam is so intense that it is necessary to reduce the current in the discharge tube by throttling it with the kinotron valve. To still further reduce the intensity we have usually raised the plate rapidly during the exposure, thus drawing a broad line on the plate of width equal to that of the main beam (see Plate 11, figs. 2 and 3). The second method may lead to error if there is any residual magnetic field deflecting the rays, for the reduced rays will probably have less energy than the original beam, and so be more easily bent. Again, if there is any electrostatic or magnetic deflection of the rays by the target the effective zero will be altered by moving it. For these reasons it is best, when the rings are clear and well developed, to use as zero their geometrical centre, but if a single crystal is being examined, or if the rings are poor, the line method is used instead. The probable error on the first method is not more than 0·25 mm. The sizes of the rings are mostly from 1 to 4 cm.

Measurement of Rings.

The rings are usually measured by dividers, the plate being held against a background of sky. Measurements can be made at night against a background of diffusely illuminated ground glass, but this is not so good for faint rings.

Measurement of Voltage.

The measurement of voltage with the induction coil was made by means of a spark gap between 5 cm. aluminium spheres. This is not very exact, and for precise work it would be much better to use a direct current source of supply, and measure the voltage by the current it produces in a high resistance in parallel with the discharge. When the Evershed and Vignolles generator was used, the potential was read on a Braun electrostatic voltmeter, which had been calibrated with an ammeter and megohm. The error in the former case is probably about 5 per cent. ; fortunately the voltage appears in the formula under a square root, so the final error is half this.

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* *V. infra* p. 649.

Measurement of "L."

The distance from the centre of the target to the plate was 40·62 cm. If the rays hit chiefly one end of the target, the proper value of L to use in equation (2) may differ from this by an amount up to half the length of the target. With the targets used, this might give a 2 per cent. error, but with care in adjustment it will be much less.

Improvements.

Possible improvements, some or all of which it is hoped to include in a new apparatus, are :—

(1) The replacement of the present wax joint, which has to be broken to change the plate, by a ground joint.

(2) An arrangement by which the plate can be brought into position without stopping the discharge, the exposure being made by springing a shutter from in front of the plate.

(3) The use of a high tension generating set instead of the induction coil. This might be expected to give a still more homogeneous electron beam, and would enable a more accurate measurement of the voltage to be made.

Summary.

An apparatus is described for examining the surface of a crystal or polycrystalline mass by the diffraction of a beam of cathode rays with a view to discovering its crystalline structure. The results of some experiments with this apparatus are described in the following paper.

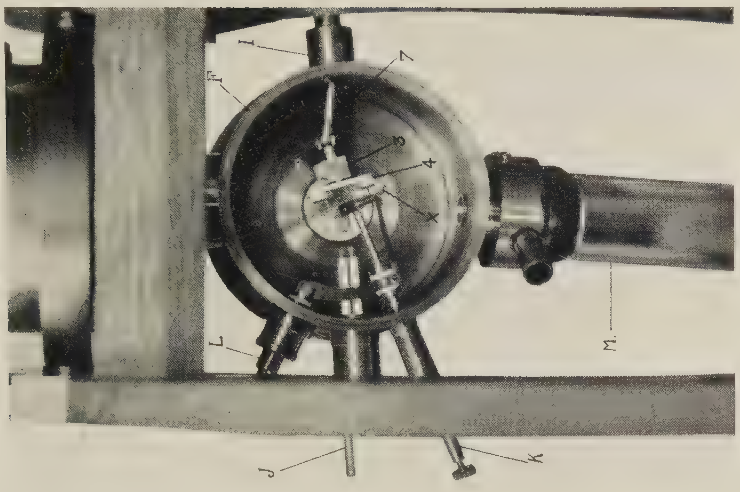
I
F
7
3
4
X
L
M
J
K

FIG. 3.

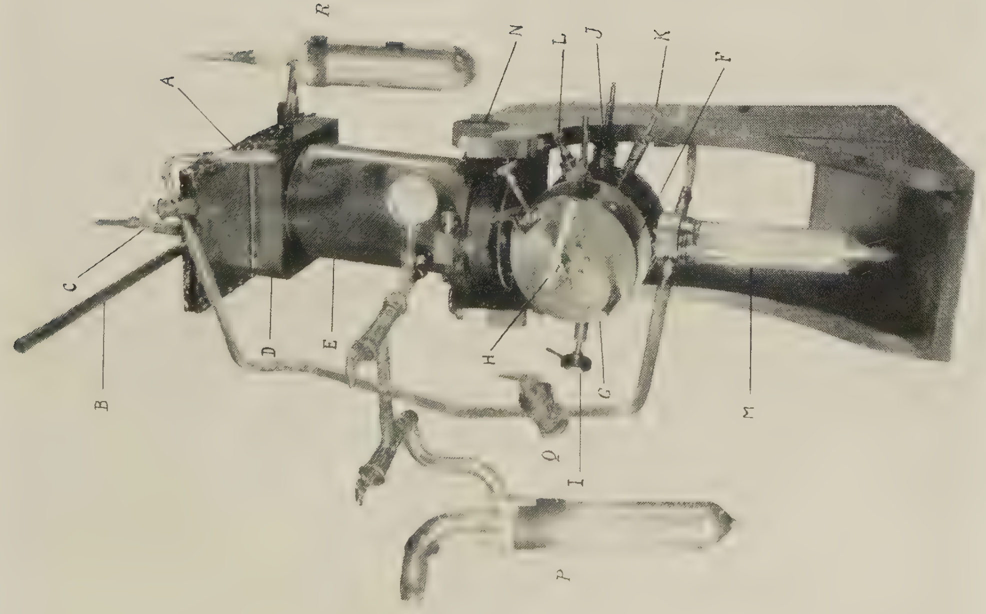
R
A
C
B
D
E
N
L
J
K
F
H
G
Q
I
M
P

FIG. 1.

(*Facing p.* 648.)

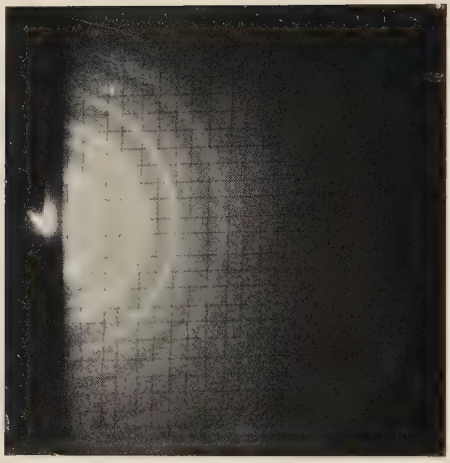

Fig. 1.—Gold spluttered on Quartz.

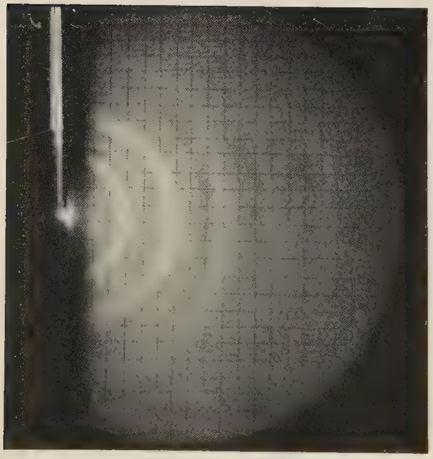

Fig. 2.—Copper heated in Air.

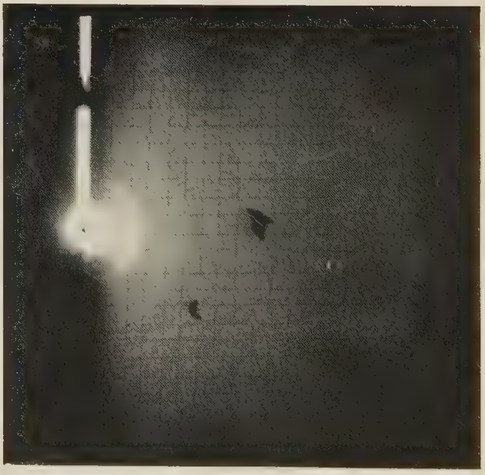

Fig. 3.—Platinum Black on Copper.

(The irregular shadows on fig. 3 are wax which has fallen on to the wire grid.)

The Analysis of Surface Layers by Electron Diffraction.

By G. P. Thomson, M.A., Professor of Natural Philosophy in the University of Aberdeen.

(Communicated by Sir Joseph Thomson, F.R.S.—Received May 6, 1930.)

[Plate 11.]

The very close correspondence which has been shown to exist between the diffraction patterns formed by cathode rays passing through thin solid films,* and the crystal structure of these films, suggests the possibility of using electron diffraction to investigate surface layers of unknown composition. This possibility was indeed indicated in Davisson and Germer's original paper† and has since been further applied.‡ These experiments have all been made with slow electrons, of energies of the order of 300 volts. With such electrons the experiments do not agree well with theory even in the case of known structures, so their application to the investigation of unknown structures involves considerable uncertainty. Further, slow electrons can only be detected photographically with very long exposures, while the electric method of detection is very cumbrous if it is desired to survey the complete diffraction pattern. For these reasons I decided to use the apparatus described in the previous paper to investigate the diffraction patterns obtained by the reflection of cathode rays from the surfaces of various solids. The discharge was generally produced by an induction coil and the energy of the rays was of the order of 30,000 volts. In a few cases, an Evershed and Vignolles direct-current generator was used giving about 6,000 volts.

In the course of the investigations, it appeared that these fast rays are uninfluenced by the thin layers of gas which are normally present on surfaces in a vacuum, or, possibly, that they temporally remove the layers by bombardment. From one point of view this is an advantage, as it is therefore unnecessary to take special precautions to degas the surfaces used, or to keep a very high vacuum. On the other hand, it limits the range of the method to the investigation of solid layers.

The following paper is an account of experiments designed primarily to exhibit the possibilities of the method as a tool of research ; up to the present I have tried to avoid being drawn aside into a close investigation of any of the tempting problems which the work has suggested. Some of these are now being made the subject of special researches, but it is hoped that the samples here exhibited may be sufficiently attractive to induce others to undertake similar investigations. The technique is not difficult, and the possible applications, especially to the study of surface chemistry, seem promising.

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* G. P. Thomson, 'Roy. Soc. Proc.,' A, vol. 117, p. 600 (1928), vol. 119, p. 651 (1928) and vol. 125, p. 352 (1929).

† Davisson and Germer, 'Phys. Rev.,' vol. 30, p. 707 (1927).

‡ Germer, 'Z. Physik,' vol. 54, p. 412 (1929); Rupp, 'Z. Electrochemie,' vol. 35, p. 586 (1929).

The targets used may be divided into two classes according to whether they are single crystals, or consist of a mass of small crystals. A single crystal should, theoretically, give a pattern of spots which should only appear strongly at certain special settings, while a polycrystalline surface should give a pattern of concentric circles, or rather circular arcs, since rather more than half the field is blocked out by the shadow of the target.

Experiment confirms these predictions in a general way. There is always, in addition to the regular pattern, a background of diffuse scattering, probably mostly electrons which have lost energy by inelastic collisions. In many cases, this background is all that appears, and the method fails, because the surface layer is either really amorphous, or, if crystalline, is constructed in such a way that diffraction at small angles is impossible. It must, of course, be realized that the penetrating power of the electrons is so small, especially at the small glancing angles used, that we are only concerned with a layer a few tens of atoms thick. To this, the method owes its value for the investigation of surface layers.

Most of the experiments were made with polycrystalline targets, and these will be described first.*

Metals.—Polished metals uniformly failed to give more than the diffuse background. I tried gold, iron, lead and copper. Aluminium with the natural oxide coating, and when etched with caustic potash, also failed, as did platinum etched in aqua regia. The same holds for metals deposited by electrolysis from aqueous solutions (gold and copper tried). On the other hand, gold deposited on a quartz surface (natural or fused) gave excellent rings (fig. 1, Plate 11), identical in pattern and size with those formed by the transmission of electrons of equal speed through thin, gold films. The same was true of gold spluttered on to molybdenum. As an indication of accuracy, the value for the size of the unit cube was found on eight plates to be 4·06, 4·05, 4·00, 4·23, 4·00, 4·11, 4·12 and 4·16, with a mean value of 4·09 A°, as against 4·06 A° from X-rays. The relative sizes of the individual rings checked with theory to an accuracy of about 1 per cent. The chief error in the relative measurements lies in the difficulty of finding accurately the centre of the circles, *i.e.*, the place where the undeviated ray would strike the plate if the target were not in the way. Where absolute measurements are concerned, the uncertainty of the measurement of voltage by a spark gap is more important.

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* For theory see previous paper (Fraser and Thomson).

Platinum Black.—In view of the importance of platinum as a catalyst, I tried precipitating platinum black from solutions of chloroplatinic acid by introducing a polished metal surface. When deposited on zinc or aluminium, the platinum black surface gave rather feeble rings, measurable with some difficulty against the strong, continuous background.

The following values were found :—

Zinc.—P = 36,200 volts, radius 11·8 mm., and P = 31,600 volts, radius 12·6 mm., taking these as due to the (111) planes the unit cube is 3·86.

Aluminium.—

	Radii (mm.).			Spacing (A°).		
P = 46,600 volts		16·2	19·9		1·42	1·16
P = 43,000 volts	10·2	16·3	20·0	2·35	1·47	1·20
	Means			2·35	1·45	1·18
	Ratio			$\frac{1}{\sqrt{3\cdot04}}$	$\frac{1}{\sqrt{8\cdot00}}$	$\frac{1}{\sqrt{12\cdot00}}$

Thus the first ring* is presumably due to (111) planes, the second to (220) and the third to (222) or (311). Of the other possible planes for a face-centred cube like platinum, (200) gives a weak reflection and the others are farther out. Taking the third ring as a mean of (222) and (311), the values of the side of the unit cube as deduced from the three rings are :—

4·06
4·10
3·98

4·05 mean.

The value for platinum found by X-rays is 3·91, and the agreement is as good as can be expected in view of the poorness of the rings.

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* The values of d for a face-centred cubic structure are $a/\sqrt{h^2 + j^2 + k^2}$, (hjk) being Miller indices of the plane which must be all even or all odd.

It is quite otherwise when the platinum is deposited on copper. In this case, the rings are very good, Plate 11, fig. 3, but do not correspond to the face-centred cubic structure characteristic of both copper and platinum. Rings were found with the following spacings :—

Voltage.	Spacings (Angstrom units).								
36,600	2·96	2·38	2·10	1·73	1·49	1·21	0·965	—	—
39,500	2·94	2·47	2·10	1·73	1·49	1·29	0·965	0·86	—
40,600	3·09	2·47	2·15	1·76	1·54	1·31	0·99	—	0·725
33,500	3·06	2·47	2·09	1·75	1·51	1·29	0·96	—	—
32,500	—	2·36	—	—	1·45	1·24	—	—	—
33,000	2·86	2·36	2·05	1·68	1·45	1·25	0·96	0·86	—
Mean spacing	2·98	2·42	2·10	1·73	1·49	1·26	0·97	0·86	—
Inverse ratio	$\sqrt{1{\cdot}99}$	$\sqrt{3{\cdot}02}$	$\sqrt{4{\cdot}00}$	$\sqrt{5{\cdot}90}$	$\sqrt{7{\cdot}95}$	$\sqrt{11{\cdot}05}$	$\sqrt{18{\cdot}8}$	$\sqrt{24}$	—

The close approximation to whole numbers under the square root show that the structure is cubic, but the presence of $\sqrt{2}$ and $\sqrt{6}$, *i.e.*, (110) and (211), shows that it is not face-centred. It is presumably some alloy of platinum and copper. The side of unit cube is 4·20 A. The appearance was the same as when the platinum was deposited on aluminium or zinc, namely, a dull black.

One experiment was made with platinum deposited on silver :—Voltage 30,100, spacings 2·60, 1·82, 1·55, 1·19. These are in the inverse ratio $\sqrt{4{\cdot}00}$, $\sqrt{8{\cdot}1}$, $\sqrt{11{\cdot}2}$, $\sqrt{18{\cdot}9}$ and presumably correspond to a face-centred cubic structure, but the side of unit cube, 5·18 A., is far too large for platinum or silver (3·91 and 4·06).

It may be mentioned that platinum deposited on copper has been found* to have no catalytic effect, while that deposited on aluminium, and to a less extent also on zinc, is very active. The explanation is clearly that in the first case the platinum is not in a normal state.

Platinized Asbestos. A number of experiments were made with platinized asbestos, a bundle of fibres being stretched across the holder in place of the usual solid target. This arrangement gave very good rings which curiously showed no trace of the fibrous structure to be expected from asbestos, nor did they in the least resemble those to be expected from ordinary platinum. Two samples were used, both prepared for use as commercial catalysts, one being said to be better than the other. No difference was detected in the diffraction patterns. I then tried the asbestos unplatinized, using a sample identical with the raw material of one of the first two. To my surprise, no difference was detectable between the patterns given by the asbestos with and without the platinum, though the latter was present to the extent of 3 per cent. or 4 per cent. and showed strongly on an X-ray photograph, besides making the asbestos dark grey in colour. The extent of the agreement is shown in the following table of spacings :—

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* Paul and Windisch, 'Ber. D. Chem. Ges.,' vol. 46, p. 4010 (1913).

Voltage.	Spacings in Angstrom units.						Sample.
Platinized—							
41,500	2·08	1·70	1·21	—	0·74	0·64	"D"
31,500	2·07	1·55	1·17	0·825	0·73	0·625	"C"
32,200	Too black to measure		1·175	0·82	0·73	0·625	"C"
Mean platinized	2·075	1·625	1·185	0·82	0·73	0·63	
Unplatinized—							
33,300	2·14	1·70	1·21	0·85	0·75	0·645	"D" unplatinized
33,500	—	1·67	1·175	0·82	0·73	0·625	"D" unplatinized
Mean unplatinized	2·14	1·685	1·19	0·835	0·74	0·635	

In addition, there were a few other lines too faint to measure accurately, but which occurred equally with and without the platinum.

This result is very hard to understand, as one would have expected the platinum to be deposited on the outside of the asbestos fibres. If that were the case, platinum alone should show in the diffraction pattern, as the electrons would not get through to the asbestos. Actually the reverse is the case, and it almost looks as if the platinum were deposited in cracks in the asbestos where the electrons could not reach it. The subject would probably repay more investigation, particularly to find if the above spacings correspond to the ordinary structure of asbestos which, I understand, is now being investigated by X-rays.

Barium Oxide.—Several attempts, all unsuccessful, were made to induce the spluttered films of gold described above to recrystallise as a single crystal. On one occasion after the film had been bombarded with electrons from a heated filament, several new rings were found, some very clear and strong. Eventually it was found that they were due to barium oxide evaporated off the filament, which was a coated one. There were four of the new rings measurable and they gave spacings of :—

3·17	1·65	1·29	1·13	(mean of two plates)
(111) 3·18	(311) 1·66	(331) 1·26	(422) 1·12	(calculated)

in the second line are given the indices and spacings of certain planes in a BaO crystal which would be expected to give strong reflection. The plane (220), which is generally strong in a structure of the type of BaO, would give a ring nearly coinciding with one of the gold rings, which were also present. If the BaO formed a continuous film, it was too thin to be visible, but it may have been present as minute specks shot off from the filament on to the target as a result of the bursting of tiny bubbles of gas.

Quartz.—After a very violent bombardment by 6,000-volt electrons from a tungsten filament, which raised the surface of the spluttered gold to near a white heat, a new set of rings appeared instead of the original gold ones. They differed from the former rings in character as well as in size, being very sharp but not very intense. The surface of the target had changed considerably in appearance; the gold appeared to have been mostly removed from the centre of the target. It seems that these new rings were due to the structure of the quartz itself, there being just enough gold left to prevent charging up, but not enough to produce appreciable diffraction. The evidence is as follows :—

Spacing corresponding to rings	2·08	1·73	1·39	1·175	0·882
Spacing of quartz planes ……	2·12	1·79	1·41	1·22	0·895
Indices of planes …………	$(20\bar{2}0)$	(0003)	$(30\bar{3}0)$	$(\bar{2}4\bar{2}0)$	(0006)

Judging from the diagram on p. 161 of Braggs's "X-rays and Crystal Structure" (1915 edition) these are the strongest lines in the region covered by the experiments, except perhaps for $(20\bar{2}1)$ with a spacing of 1·67, which would hardly be distinguishable from (0003). The piece of quartz used in this experiment was an old piece of fused quartz, clear and with a fairly flat surface, but not optically worked.

Oxidized Copper.—While a polished copper surface gives no rings which can be referred to the metal itself, very faint rings are observed if the specimen has been in air at atmospheric pressure for even $\frac{3}{4}$ hour. If it is left in air overnight, the rings, though still rather blurred against the continuous background, become measurable. Their intensity and clearness are greatly increased by heating the metal gently in an electric furnace till the surface shows a marked change of colour. The same occurs with a surface of copper electrolytically deposited. If the heating is afterwards continued till the surface passes through several colour changes, the clearness of the rings greatly diminishes. The sizes of the rings were found to be in the (mean) ratio of $\sqrt{2\cdot99} : \sqrt{4\cdot09} : \sqrt{11\cdot0} : \sqrt{18\cdot8}$.

The ratios suggest the familiar face-centred cubic structure for which the mean value of the side of unit cube would be 4·21 A. The structure of Cu_2O (cuprite) is known* ; the copper atoms lie on a face-centred cubic lattice, the oxygen atoms on a body-centred cubic lattice, both of side 4·26 A. There should be a very faint $\sqrt{2}$ ring and one at $\sqrt{18}$, besides the usual face-centred cubic series ($\sqrt{3}$, $\sqrt{4}$, $\sqrt{8}$, $\sqrt{11}$, $\sqrt{12}$, $\sqrt{16}$, $\sqrt{19}$, $\sqrt{20}$). The agreement is reasonably satisfactory.

If a polished copper block is left on a red hot block of brass or copper till it turns colour, then removed and allowed to cool in air, it gives in the diffraction apparatus a totally different set of rings from the above, though the treatment is so similar. The new rings are among the finest I have obtained, and the values of the spacings calculated from them show the accuracy of the method in favourable circumstances (see Plate 11, fig. 2).

Over 20 rings were clearly visible, of which those of smallest size gave the following spacings :—

Voltage.	Spacing in Angstrom units (corrected for relativity).								
6,250	2·68	2·49	2·28	—	—	—	—	1·38	1·34
6,400	2·68	2·49	2·28	—	—	—	—	1·385	1·345
32,000	2·71	2·49	2·22	1·83	1·71	1·59	1·50	1·365†	
29,000	2·71	2·47	2·26	1·88	1·71	1·595	1·52	1·38†	
? (values relative only)	2·70	2·48	2·27	1·87	1·70	1·59	1·51	1·365†	
Mean	2·70	2·48	2·26	1·86	1·71	1·59	1·51	1·385	1·345

Voltage.	Spacing in Angstrom units (corrected for relativity).								
6,250	—	—	—	—	—	—	—	—	—
6,400	—	—	—	—	—	—	—	—	—
32,000	1·30	1·17	1·10	1·00	0·954	0·9315	0·890	0·858	—
29,000	1·31	1·165	1·105	1·02	0·977	0·950	0·906	0·858	—
? (values relative only)	1·28	1·15	1·075	1·00	0·945†		0·89	0·856	—
Mean	1·30	1·16	1·09	1·01	0·965	0·94	0·895	0·857	—

† Doublet not resolved.

It has not so far been possible to deduce the structure corresponding to these spacings, which were obtained with two specimens. It is not that of tenorite (CuO) given by Niggli.* Further work is in progress with the hope of discovering what determines the crystal form taken up by heated copper, and what the chemical composition of the second form may be.

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* Greenwood, 'Phil. Mag.,' vol. 48, p. 654 (1924).

Copper Sulphide.—If a polished copper block is dipped in a dilute solution of "liver of sulphur," the surface changes, showing the colours of thin films. Experiments were made with a surface of this kind which showed the red of the second order. The rings were fair and showed the following spacings (mean of three plates):—

	2·86 f.	2·34 f.	1·92 s.	1·64 m.	1·22 m.	1·06 m.
Inverse ratio	$\sqrt{3\cdot6}$	$\sqrt{5\cdot4}$	$\sqrt{8\cdot00}$	$\sqrt{11\cdot0}$	$\sqrt{19\cdot8}$	$\sqrt{26\cdot5}$

f. = faint; s. = strong; m. = medium.

Cu_2S has a structure of the CaF_2 type; the sulphur atoms lie on a face-centred cube of side $a = 5\cdot59$, while the copper atoms are at the centres of the eight cubes of side $a/2$ into which the main cube can be divided. Taking the copper atoms only, there are spacings inversely as $\sqrt{4}$, $\sqrt{8}$, $\sqrt{12}$, ... $\sqrt{4n}$, while the sulphur atoms would give rings, probably faint, at $\sqrt{3}$, $\sqrt{11}$, $\sqrt{19}$, $\sqrt{27}$. Unless the second ring $\sqrt{5\cdot4}$ is due to an impurity, the surface cannot therefore be Cu_2S, though the absolute side of the (assumed) unit cube agrees fairly well, namely, 5·44 against 5·59.

Copper Selenide and Telluride.—Similar experiments were made with selenium and tellurium, the copper being dipped into dilute solutions of SeO_2 in water, and of TeO_2 in dilute hydrochloric acid respectively. The mean spacings found were:—

Selenide			2·31 f.	1·95 s.	1·68 m.	1·26 f.	1·08 f.	
Inverse ratios			$\sqrt{5\cdot7}$	$\sqrt{8\cdot00}$	$\sqrt{10\cdot8}$	$\sqrt{19\cdot2}$	$\sqrt{26\cdot2}$	
Telluride	4·06 f.	3·08 m.	2·38 s.	1·95 m.	1·47 f.	1·25 m.	1·15 f.	0·95 f.
Inverse ratios	$\sqrt{2\cdot7}$	$\sqrt{4\cdot8}$	$\sqrt{8\cdot00}$	$\sqrt{11\cdot7}$	$\sqrt{21}$	$\sqrt{29}$	$\sqrt{34}$	$\sqrt{50}$

It is fairly certain that the three are analogous compounds, and the presence in all of a ring analogous to the second of the sulphur compound makes it unlikely that the latter is due to an impurity.

These surface layers are of practical interest as finishes for copper articles. Further work on their structure is in progress at Cornell University.

Iron Oxide.—Polished iron gives no rings, but with electrons of 6,000 volts energy one photograph showed a very diffuse spot roughly in the position of specular reflection. This may possibly be evidence of a gas layer; if so, it is the only one so far obtained. If the iron be allowed to rust in water and then tested in the electron camera, a fine set of rings appears which can be easily seen on the Willemite screen. The mean spacings were :—

---

* Niggli quoted by Bragg, "X-rays and Crystal Structure," p. 301.

Observed spacing	3·15	(2·79)	2·43	2·22	(1·93)
Spacing for Fe_2O_3	3·69	2·69	2·51	2·22	2·05
Dimmed surface (see below)				(2·23)	
Observed spacing	1·84	1·64	1·455	1·31	1·14
Spacing for Fe_2O_3	1·845	1·69 1·60	1·49 1·45	1·31	1·119 to 1·11
Dimmed surface (see below)	1·785		1·42	1·31	1·13

The figures in plain brackets were from one plate only. The third and fourth rings were not fully resolved, so their measurements are somewhat uncertain.

The values for Fe_2O_3 are calculated from measurements by Hedvall* of powder photographs, checked by the values of the crystal elements given by Pauling and Hendricks.† There is excellent agreement except for the first ring. This is very small, so that an error in the position of the centre would cause a large percentage change, but the difference seems to be too great for this to be the explanation, and it is more likely to be due to slight charging up of the target or to magnetic action. The error is of the order of 0·75 mm. on the plate.

Experiments were also made on a surface of iron, originally polished, then dipped in nitric acid of sufficient strength to make the iron passive, and finally washed in distilled water and dried. The surface then showed a slight dimming of its original polish. It gave good rings, both with the 6,000-volt generator and with the induction coil, only slightly less clear than those given by the iron surface covered with thick rust. The mean spacings are given in the third line of the table above. It will be seen that they agree well with the structure of Fe_2O_3, the inner rings not being clear enough to measure. It is remarkable that a layer which was hardly visible should give such a well-defined pattern. The experiment was repeated with another surface which gave the same result. It is unlikely that these surfaces were passive when tested in the electron camera, as drying the water generally destroys the passivity. However, by treatment with suitable solutions it is possible to get a dry, passive surface, and it would be of interest to see if this gives rings.‡

Aluminium Oxide.—A piece of aluminium covered with the usual film which forms in air failed to give any definite rings. It had been cleaned with petroleum ether and alcohol.

Lead.—A piece of lead treated similarly to the aluminium above equally failed to give rings, nor was a specimen polished with oil on a sheet of paper any more successful. Lead freshly cut and heated to about 100° C. in air for some time also gave nothing. When, however, the lead was heated to near the melting-point for about an hour it gave measurable rings. These were not sufficiently numerous on the one specimen tested to enable the structure to be determined.

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* Hedvall, 'Z. Anorg. Chem.,' vol. 120, p. 327 (1922).

† 'Jour. Amer. Chem. Soc.,' vol. 47, p. 781 (1925).

‡ See note attached.

[*Note added in proof.*—I have since succeeded in keeping the iron passive throughout the whole experiment. In these circumstances the rings corresponding to Fe_2O_3 do not appear, so those in the earlier experiments must have been caused by action after the iron had ceased to be passive. Instead, a number of rather faint spots were found which agree well with the structure of ordinary iron, spots being formed instead of rings presumably because only a few crystals of iron are effective. The same pattern occurs if the iron is not passive, being the only instance so far found of a pattern from an etched metalic surface. It appears, therefore, that if the passivity of iron is due to a surface layer it must be one so thin as to elude even the sensitive test of electron diffraction. In some other experiments on iron attacked by nitric acid I have found a layer showing the structure of Fe_3O_4.]

Discussion.

It is hoped that enough examples have been given above to show the possibilities of the method as a tool of research. Apart from particular problems, a number of questions of a general nature are suggested by the experiments we have described. One of the most important is: what are the conditions which determine whether or not a surface will give a diffraction pattern? The first requirement is clearly that the actual surface must be crystalline, for the electrons can only penetrate a very small depth, especially at a glancing angle of only 1° or 2°, without experiencing an inelastic collision which disqualifies them from forming a diffraction pattern. No doubt the reason that polished metals fail to give rings is that their surface is covered with an amorphous layer of super-cooled liquid (Beilby layer). It is less obvious why an etched metal surface should give nothing (*e.g.*, aluminium and platinum). The reason may be that such a surface consists of a succession of pits and pyramids with flat, crystal surfaces for their boundaries. If the dimensions of the pyramids are large compared with the penetrating power of the electrons, it will rarely occur that an electron can pass in at one face and out at another, after reflection from a crystal plane (not a face) inside. Thus the only chance of getting strong reflection would be for the electron to enter and leave the same crystal surface. For this the surface must make an angle with the ray not greater than the glancing angle of selective reflection, whether the reflecting plane is the crystal surface itself or some plane in the crystal oblique to it.* Now, the angle in question is small so that a reflecting facet will present a target to the rays small compared with its true area; it is therefore very improbable that the first surface which the ray strikes will lie within the required angle. A favourable arrangement for the formation of rings is a surface covered with *small* lumps, rather like a field of cornstooks on a miniature scale. The lumps must be small enough to give an electron a chance of going right through without making an inelastic collision. In this case, if the angle for selective reflection is θ and the "tolerance" $\delta\theta$, the chance of finding the first crystalline lump in the right attitude is $p \cos\theta\,\delta\theta$, where p is the number of ways the crystal can be turned to give a plane of the same spacing.

In the former case, if for simplicity we suppose the surface to be formed of a number of equal pyramids disposed at random, the projected area of all surfaces with which the rays make an angle less than θ is

$$\frac{\int_0^{\theta} \sin\theta \cos\theta \, d\theta}{\int_0^{\pi/2} \sin\theta \cos\theta \, d\theta} = \sin^2\theta$$

of the whole cross section of the beam. If the electron hits such a surface first, it has a chance $\cot\theta\,.\,\delta\theta$ of being reflected from the surface face, and $\cos\theta\,.\,\delta\theta\,(p-1)\,q$ of reflection from some other equivalent face.† The total chance of reflection is $\cos\theta\,.\,\delta\theta\,[\sin\theta + \sin^2\theta\,.\,(p+1)\,q]$, which if θ is small is much less than $\cos\theta\,.\,\delta\theta\,.\,p$, the chance when the surface is covered with small lumps.

It is a general rule that a polished surface which has recently been attacked chemically gives some kind of rings. The failure of aluminium and lead covered with the ordinary protective layer of oxide to give an effect may be due to the layers having been old. In general, the clearness of the rings tends to diminish with the age of the specimen, perhaps indicating that larger crystal units are formed.

In the above argument, we have not considered the effect of refractive index.

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* It is assumed that the angle between any two important reflecting planes, of which the surface will be one, is less than the angle of selective reflection.

† Here q is a numerical factor, never large compared with unity, which depends on the angles between the p equivalent faces.

As shown in an earlier paper,* the refractive index corresponding to the probable value of the inner potential of a metal would have a large effect on the deviation of an electron which was reflected from a crystal plane *parallel to a face surface.* The effect is due to the smallness of the angle of incidence, and would not occur to any appreciable extent if the surfaces through which the electron passed at entrance and exit were not closely parallel to the plane of reflection. No effect of refractive index has been observed in these experiments, and this is strong evidence for supposing that (*e.g.*) the gold deposited by spluttering is in the form of little lumps with irregular surfaces, through which the electrons pass, rather than crystals with extended flat surfaces. Or at least, that enough of the former are present to cause the observed diffraction.

If the target is not of the same material as the case of the instrument, there will be a difference of potential between a point just outside the surface of the target and one just inside the case. The field of force corresponding to this will exert forces on the beam of electrons, but for 1 volt the distance on the plate is only of the order 10^{-4} cm., which is quite negligible.

Some experiments were made with crystals of calcite and galena giving results in qualitative agreement with the work of Emslie.† Rocksalt gives well marked diffraction patterns which are being further investigated.‡

A considerable part of the work described above was done at Cornell University, U.S.A., where I was Baker Lecturer, and my sincere thanks are due to the authorities there, and especially to Prof. Dennis, for the excellent facilities provided, and also to Mr. H. R. Nelson, M.A., for his capable assistance in a number of the experiments. My thanks are also due to Mr. J. D. McKay, whose quickness and skill have been immensely valuable in all these experiments.

Summary.

(1) Using the apparatus described in the preceding paper, it was found that the surfaces of many solids give diffraction patterns with electrons. These patterns are caused by the crystalline structure of the surface and in several cases enable this to be determined.

(2) Owing to the slight penetrating power of the electrons, this method affords a means of investigating surface layers, comparable to that provided by X-rays in the case of matter in bulk.

(3) The following are some surfaces which showed measurable diffraction

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* 'Phil. Mag.,' vol. 6, p. 939 (1928).

† Emslie 'Nature,' p. 977, vol. 123 (1929).

‡ See 'Nature,' July 12, 1930. [Note added in proof.]

rings corresponding to a polycrystalline structure, and the nature of this structure in so far as it could be determined from these rings :—

Surface.	Structure.
Gold spluttered on quartz	Gold.
Ditto, bombarded from a filament coated with BaO.	Gold and BaO.
Ditto after severe bombardment	Quartz.
Platinum black deposited on Zn or Al	Platinum.
Platinum black deposited on Cu	A cubic structure *not* Pt or Cu.
Platinized asbestos	The same complex structure, not identified.
The same asbestos unplatinized	
Copper heated in air, 1st method	Cu_2O (cuprite).
Copper heated in air, 2nd method	A complicated structure *not* cuprite or tenorite (CuO).
Copper dipped in sulphide solution	Probably not Cu_2S.
Copper dipped in selenide solution	Not Cu_2Se.
Copper dipped in telluride solution	Not Cu_2Te.
Iron rusted	Fe_2O_3.
Polished iron, dipped in strong nitric acid, washed and dried.	Fe_2O_3 (see note p. 658).

(4) Polished and etched metals gave no pattern, nor did electro-deposited gold or copper.

(5) It seems that almost any smooth surface which has recently undergone chemical change will give a diffraction pattern corresponding to its new crystal structure.

(6) Single crystals of calcite, galena and rocksalt gave diffraction patterns of spots.

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